

CONFIGURATION, CONFORMATION AND SPIN IN RADICAL PAIRS

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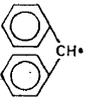
COUPLING RATES OF FREE RADICALS

Many free radicals react with one another fast enough so that their coupling can compete with the diffusion process. This is the basis of the well-known "cage effect" which allows freshly generated radical pairs to combine with one another and escape the action of efficient scavengers present in the solution. The speed of radical coupling raises the hope of being able to observe the competition with other processes too fast for normal measurement. Among these processes are intramolecular rotation, rotation relative to the surrounding solvent molecules, conformational changes involving several cooperative intramolecular rotations, and the reorientation of electron spins. Rate constants for bimolecular combination of free radicals which have been measured range from $3600\text{M}^{-1}\text{sec}^{-1}$ for triphenylmethyl radicals¹ to $3.6 \times 10^{10}\text{M}^{-1}\text{sec}^{-1}$ for methyl radicals². In many intermediate cases of interest direct measurements of the rates of radical-radical combination have not been made, but accurate measurements of cage effects are available. Taking the interpretation of the cage effect at its face value, we should be able to make order-of-magnitude estimates of the rate constants for radical-radical coupling from these cage effect measurements. One of the most useful sources of such cage effect measurements is the type of experiment in which a symmetrical aliphatic azo compound is decomposed by heat or by light in the presence of a scavenger of demonstrated efficiency. Those free radicals which survive the repeated collisions with their original partners in the "solvent cage" are quantitatively captured by the scavenger. When the number of radicals so captured is found to be a constant fraction of the number produced from the azo compound, regardless of the excess of the scavenger and of the concentration of the substrate, the relative numbers of radicals scavenged and coupled are considered to measure the relative rate constants of diffusion and of coupling. Both rate constants depend upon the solvent so that cage effects for a given radical pair measured in a series of familiar solvents may vary over a range of about twofold. The diffusion constants of the free radicals have usually been neither measured nor approximated experimentally. If we were to assume that the diffusion rates of the free radicals in *Table 1* are roughly proportional to the inverse square roots of their molecular weights, we might then conclude that the figures in the last column of the Table represent an approximation to the relative rate constants for coupling of the radicals in question.

The result is at first sight surprising. As we go from the small and unstabilized methyl radical to the large benzhydryl radical with not less than

25 kcal of resonance energy, the rate constant for coupling of such radicals appears to decline by only a factor of about 10. The addition of a third phenyl to make triphenylmethyl must then at one stroke accomplish the remaining millionfold reduction in coupling rate constant which has been

Table 1. Cage effects in decomposition of azo compounds

<i>R</i> in $RN=NR$	% Cage Effect	$\frac{\text{Coupling}}{\text{Diffusion}}$	$\frac{\text{Coupling}}{\text{Diffusion}} \times (MW)^{-1/2}$	Reference
CH ₃ 	78 (benzene, 25°)	3.5	0.91	2
	21.5 (benzene 62.5°) 26 (toluene 62.5°) 30 (cumene, 62.5°)	0.27	0.025	3
	54-57 (benzene, 34°)	1.25	0.095	4
	27 (toluene, 40°)	0.37	0.034	5

reached by triphenylmethyl. The cage effect results are totally incompatible with the reported rate constant of only 7×10^6 for coupling of the α -tetralyl radical⁶ unless diffusion rates in solution are an enormously steeper inverse function of molecular weight than has been suspected.

There are two kinds of indications that the orders of magnitude for coupling rate constants indicated by the cage effect may be correct. Stuart models show a large and sudden increase in steric hindrance to central carbon-carbon bond formation as we pass from the benzhydryl to the triphenylmethyl radical. There is evidence of long standing⁷ that the effects of hindering *ortho* substitution on the dissociation constant of a dissociable ethane can be much more spectacular than a substitution elsewhere which only affects the resonance energy of the free radical. Furthermore, there are numerous completely stable, non-associating free radicals known which are extremely efficient scavengers for short-lived free radicals. From the linear decline of concentration of galvinoxyl in the presence of decomposing azobisisobutyronitrile or di-*t*-butyldiperoxyoxalate^{8†} it can be shown that the rate constant of cross coupling between this stable free radical and the unstable ones must be not less than 10^6 l./mole sec. A resonance energy of 20-30 kcal will therefore not prevent a radical from coupling at a high and even diffusion-controlled rate provided that the coupling can form a normally strong and unhindered carbon-carbon bond.

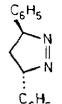
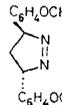
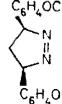
† In the scavenging experiments of this paper⁸, a rate constant less than 10^5 sec⁻¹ for reaction of iodine with cyanoisopropyl radicals would require a departure from zero-order kinetics toward the end of the scavenging period, where in fact zero-order linearity was maintained. Galvinoxyl scavenges cyanoisopropyl faster than iodine does by at least a factor of 10.

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STEREOCHEMISTRY OF RADICAL COUPLING

It appears that the series of substituted azo- α -phenylalkanes should offer great flexibility in the choice of substrates for studying the competition of radical reunion with diffusion, configurational and conformational change, and rotation in freshly formed radical pairs. In at least 60 instances azo compounds with asymmetric carbon atoms adjacent to the nitrogen have been prepared and decomposed. In the special case of the pyrazolines (Table 2) substantial degrees of stereospecificity have been observed in the thermal decomposition and especially in the photo-decomposition at or below room temperature of stereoisomers differing in their configurations adjacent to the azo group. In view of evidence that the pyrazolines undergo concerted decomposition by way of 1,3-biradicals⁹ these results seem to establish the

Table 2. Decomposition of pyrazolines

Azo Compound	Temperature (°C)	Products of Decomposition (%)		
		<i>cis</i>	<i>trans</i>	Reference
 (<i>trans</i>)	80°	11	89	<i>a</i>
 (<i>trans</i>)	100° 13° (photo)	6.7 0.7	93 99.3	<i>b</i> <i>b</i>
 (<i>cis</i>)	100° 13° (photo)	43 57	57 43	<i>b</i> <i>b</i>
 (<i>trans</i>)	155-165° 35° (photo)	45 7.5	55 92.5	<i>c</i> <i>c</i>
 (<i>cis</i>)	155-165° 35° (photo)	59 98.5	41 1.5	<i>c</i> <i>c</i>
 (<i>trans</i>)	220°	72.6	25.4	<i>d</i>
 (<i>cis</i>)	220°	33.2	66.1	<i>d</i>

^a C. G. Overberger, R. E. Zangaro, and J.-P. Anselme. *J. Org. Chem.* **31**, 2046 (1966).

^b C. G. Overberger, N. Weinshenker, and J.-P. Anselme. *J. Am. Chem. Soc.* **86**, 5364 (1964).

^c T. V. van Auken and K. L. Rinehart. *J. Am. Chem. Soc.* **84**, 3736 (1962).

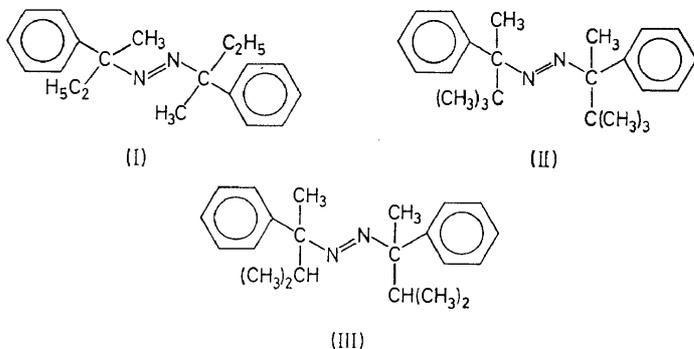
^d R. J. Crawford and A. Mishra. *J. Am. Chem. Soc.* **87**, 3768 (1965).

ability of radical coupling to compete with intramolecular rotation in a case where radical diffusion is prevented by the cyclic nature of the starting material. This behaviour is also consistent with that of biradicals intermediate in certain cycloadditions¹⁰, where substantial but incomplete stereoequilibration precedes ring closure. The present work was undertaken to ascertain whether such effects may also be observed where the two free radicals are held together only by the forces prevailing in the solvent cage.

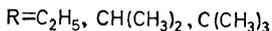
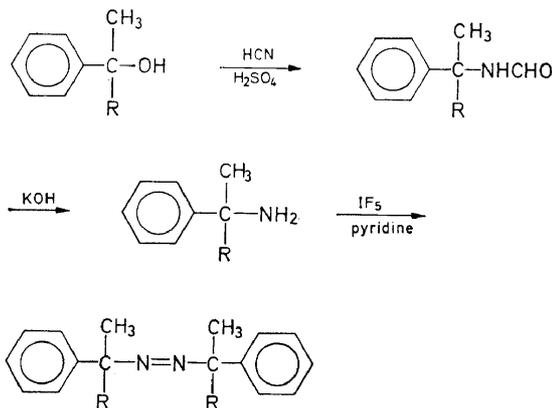
Berezin¹¹ in 1963 decomposed azobis-*a*-phenylethane (probably nearly pure *meso*, recrystallized from 95 per cent ethanol, m.p. 72–73°) in the presence and absence of thiol scavengers. The yields of *meso*- and *DL*-2,3-diphenylbutanes were nearly equal with the *meso* predominating slightly in both scavenged and unscavenged decompositions at 115°.

A SOURCE OF ASYMMETRIC RADICALS

Since azo compounds which yield tertiary radicals have become available by the useful reaction of Stevens^{12, 5}, we investigated azobis-2-phenylbutane (I), azobis-2-phenyl-3,3-dimethylbutane (II), and azobis-2-phenyl-3-methylbutane ("AMPB") (III), as starting materials for investigating the



behaviour of tertiary radical pairs. Compound (I) was prepared by the sequence shown below:



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One of the diastereomers of the azo compound was obtained pure and the other in 70 per cent predominance by fractional crystallization. Unfortunately, no way was found for accurate determination of the isomeric composition of the 3,4-dimethyl-3,4-diphenylhexane produced by decomposition of (I). For this reason the further study of (I) was abandoned.

The attempt to prepare (II) was abandoned after it was established that the reactions of phenylmethyl-*t*-butylcarbinol under acid conditions led to complete neopentyl rearrangement and that the reactions involved in an approach through α -phenyl- α -*t*-butylpropionic acid were extremely hindered and proceeded in very poor yield.

Compound (III) was prepared by the sequence shown above. The hindered formamide was hydrolyzed by heating at 170° with potassium hydroxide in triethyleneglycol for 30 min. Recrystallization of (III) from ethanol-ether and from ether gave pale yellow-green crystals melting at 40–40.3° and having the n.m.r. spectrum shown in *Figure 1*. A sample of

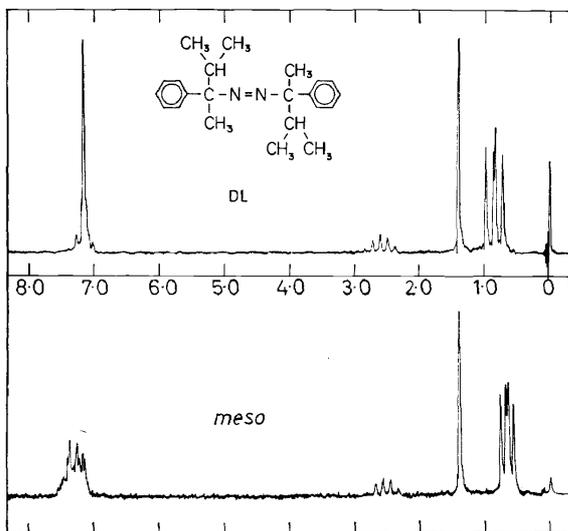


Figure 1. N.m.r. spectra of the diastereomers of azobis-3-methyl-2-phenyl-2-butane (III).

3-methyl-2-phenyl-2-butylamine, resolved with D-tartaric acid to an observed optical rotation $\alpha_{436} = -37.30^\circ$ (homogeneous, 1 dm), was coupled with iodine pentafluoride to a sample of azo compound (III) having the optical rotations shown in *Table 3*. The n.m.r. spectrum of this optically

Table 3. Optical rotation of (+) azo-3-methyl-2-phenyl-2-butane in CCl_4

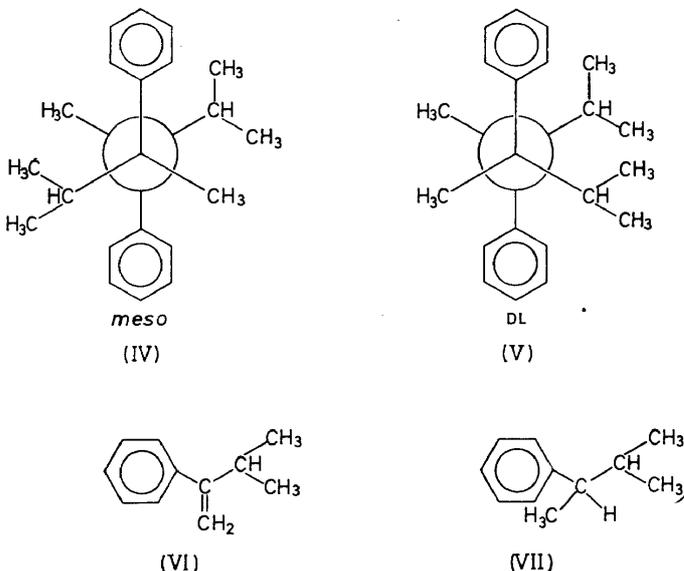
λ ($m\mu$)	Rotation	Concentration (mg/ml)	$[\alpha]$
578	+ 0.138°	26.1	+ 5.29°
546	+ 0.254°	26.1	+ 9.74°
436	+ 4.065°	26.1	+ 156°
365	- 0.570°	1.30	- 439°

active liquid azo compound, taken in conjunction with that of the crystalline *meso* sample, led to the conclusion that the optically active [(+)]III contained about 20 per cent *meso* isomer.

Comparison of the spectra of the crystalline inactive and the liquid optically active azo compound permitted identification of the n.m.r. signals of the *meso* and DL isomers. Thereafter, further optical resolution was unnecessary, since the stereochemical behaviour of the radical pairs from decomposition of the azo compound could be followed with the use of *meso* and DL samples.

DECOMPOSITION OF AMPB (III) IN SOLUTION

Thermal or photochemical decomposition of (III) in all solvents from 0 to 100° gave mixtures containing *meso*- (IV) and DL (V)-3,4-diphenyl-2,3,4,5-tetramethylhexanes (TMDPH), α -isopropylstyrene (VI), and 3-methyl-2-phenylbutane (VII). The n.m.r. spectrum of the coupling product showed two methyl singlets of similar intensities and four methyl



doublets as shown in Figure 2. Through a fortunate circumstance described below it was possible to obtain the pure *meso* compound and assign the peaks in the n.m.r. spectrum to their corresponding diastereomers. As shown in Figure 3, the DL- and *meso*-diphenyltetramethylhexanes are obtained in nearly equal amounts from *meso*, DL, or optically active azo compounds, the ratio showing very little concentration dependence. The ratio of disproportionation to coupling of the radicals increases with rising temperature at such a rate as to indicate that the activation energy for disproportionation is about 2 kcal greater than that for coupling while the activation energies for *meso* and DL couplings are not accurately distinguishable.

A solution of *meso*-azo-3-methyl-2-phenyl-2-butane (AMPB, III) in benzene was made about 3 M in thiophenol, a good scavenger of free radicals.

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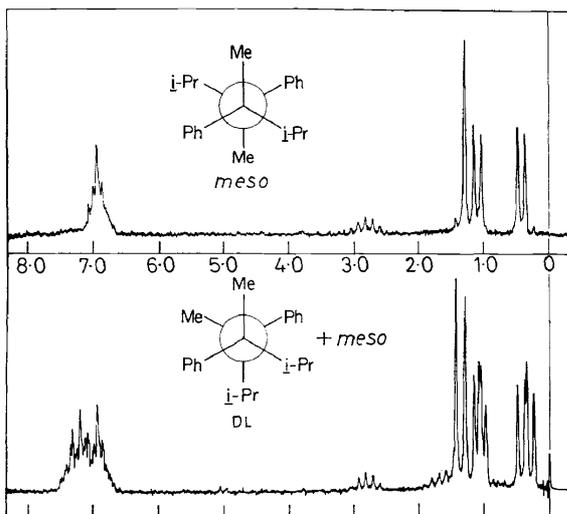


Figure 2. N.m.r. spectra of *meso*- and DL-2,3,4,5-tetramethyl-3,4-diphenylhexane.

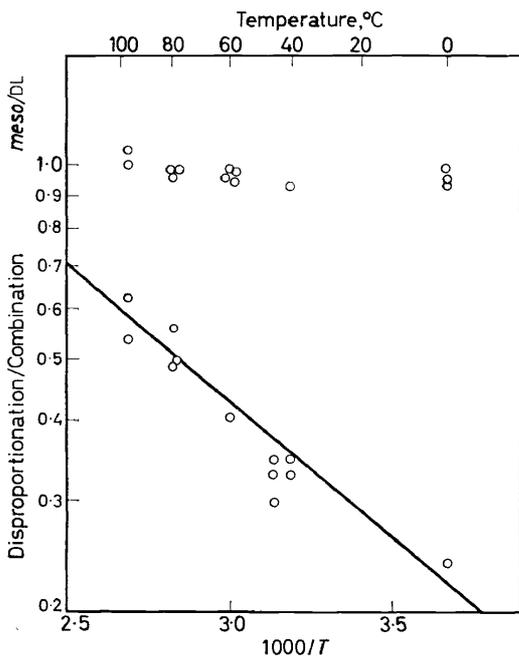
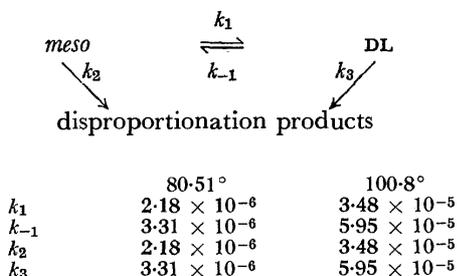


Figure 3. Ratios of decomposition products from azobis-3-methyl-2-phenylbutane (III) in chlorobenzene solution. Thermolysis at the highest three temperatures, photolysis at the lowest two temperatures.

After degassing and thermal decomposition at 62° in a sealed n.m.r. tube, the product contained no detectable α -isopropylstyrene and only an estimated 1 per cent of the coupling product, 3,4-diphenyl-2,3,4,5-tetramethylhexane. Therefore, the β -methyl group in the 2-phenyl-3-methyl-2-butyl radical has reduced its rate of coupling to the point where its cage recombination at 62° has become too small to measure with certainty. The products which we are observing in the unscavenged runs also are the products of reaction of radicals which have escaped from their original partners and have of course had time to assume random orientation in the solution before combining.

THERMAL EQUILIBRATION AND DISPROPORTIONATION OF TMDPH (IV AND V)

In exploratory experiments it was found impossible to put 3,4-diphenyl-2,3,4,5-tetramethylhexane (IV or V) through vapour phase chromatography without the continuous appearance of a much more volatile substance. Kinetic experiments showed that at 80° and 100° samples of this hydrocarbon in aromatic solvents undergo thermal disproportionation to α -isopropylstyrene and 2-phenyl-3-methylbutane (VI and VII). Samples of *meso* hydrocarbon and samples of DL hydrocarbon during decomposition approach a steady state composition with respect to the diastereomers corresponding to *meso*/DL \cong 1.85 at 80° and 2.2 at 100°. A mixture originally having this composition decomposes at an overall first order rate, the diastereomeric (IV) and (V) remaining in the same proportion throughout the reaction. Figure 4 shows the changing concentrations of the two diastereomeric coupling products and of the products of disproportionation during heating of an initially pure sample of *meso*-3,4-diphenyl-2,3,4,5-tetramethylhexane. Combination of information from several sources makes it possible to assign rate constants in the simple scheme as follows:



These rate constants afford a value for the activation energy for disproportionation of 36.7 kcal for the *meso* and 38.4 kcal for the DL isomer. This value lies midway between the activation energies found by Ziegler¹³ for dissociation of dicumyl (50 kcal) and of tetracyclohexyldiphenylethane (21 kcal). A similar behaviour of 2,3-diphenylsuccinonitrile diastereomers on heating has been reported recently¹⁴.

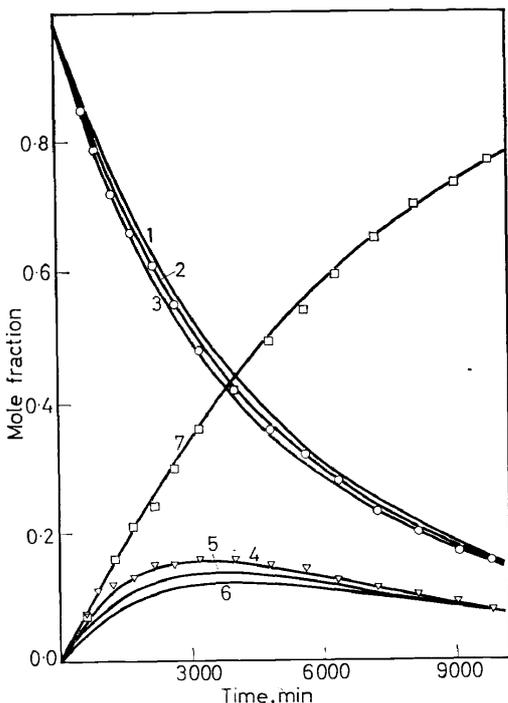


Figure 4. Changing composition of solutions of *meso*-TMDPH (IV) in chlorobenzene heated at 80°. Falling curves: IV. Circles, experimental points. Assumed values for k_1 , k_{-1} , k_2 , and $k_3 \times 10^6$: curve 1, 1.40, 1.98, 2.24, 3.17; curve 2, 1.70, 2.48, 2.22, 3.24; curve 3, 2.18, 3.31, 2.18, 3.31. Lower rising curve: V. Assumed k_1 , k_{-1} , k_2 , and k_3 : curve 4, 2.18, 3.31, 2.18, 3.31; curve 5, 1.70, 2.48, 2.22, 3.24; curve 6, 1.40, 1.98, 2.24, 3.17. Upper rising curve (curve 7), α -isopropylstyrene (VII), consistent with all three sets of k 's.

THE CAGED STATE IN FROZEN SOLVENTS

(a) Coupling and disproportionation

Hiatt and Traylor¹⁵ have recently shown that a cage effect which in benzene is too small to be measured can be magnified by the choice of increasingly viscous solvents so that in Nujol the cage effect reaches 70 per cent. A frozen matrix may be regarded as the ultimate limit of a viscous solvent in which a maximum should be reached in the probability of geminate recombination of free radicals relative to their diffusion, internal rotation, or rotation with respect to the surrounding medium. *meso*-AMPB was therefore decomposed photolytically in methylcyclohexane glass at liquid nitrogen temperature. The products were (IV) with substantial amounts of (VI) and (VII). In contrast to all the photolysis and thermolysis products obtained in liquid solutions, the product upon recrystallization yields a single isomer of the coupling product. This was the source of the pure *meso*-TMDPH (IV) used as an n.m.r. standard for analysis of the diastereomeric mixtures and as a starting material for the isomerization and disproportionation studies described earlier. It is assumed that the single isomer of coupling product obtained from *meso*-AMPB has the *meso* configuration and that the other isomer obtained in high predominance from a mostly

DL-AMPB is the DL coupling product. It is evident from these experiments that the radical pair produced in a frozen medium at liquid nitrogen temperature has the properties anticipated for a radical pair in a cage in which direct interaction of the two radicals by either combination or disproportionation becomes faster than either diffusion or rotation of the free radicals about any axis perpendicular to the line joining them.†

Since this behaviour lies at the opposite extreme from that in any liquid solution, a series of experiments under intermediate conditions was performed. With *meso*-AMPB as starting material in benzene it was found that the *meso*/DL ratio in the coupling product increases sharply and steadily with the distance below the melting point of the solvent as shown in *Figure 5*.

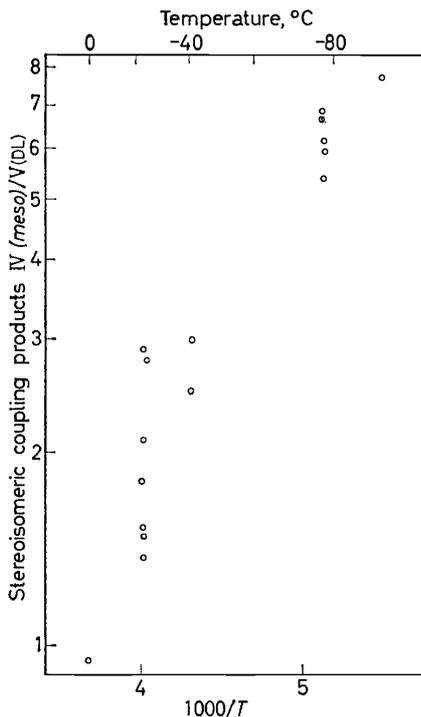


Figure 5. Effect of freezing on ratio of stereoisomeric coupling products IV (*meso*) and V (DL) from photolysis of benzene solutions of *meso*-AMPB (III).

At the same time the ratio of disproportionation to coupling of the radicals increases sharply but in benzene appears to pass through a maximum as the temperature is lowered (*Figure 6*). Toluene, which freezes at a much lower temperature than benzene, shows a much less pronounced effect on each ratio, and chlorobenzene occupies an intermediate position.

† Actually, as is shown below, the recombination of at least some of the radicals at -196° is essentially totally frozen out. The formation of *meso*-TMDPH must therefore occur on warming the photolyzed glass. The conclusion to be drawn from the stereospecific coupling of radicals is that of the competing processes of product formation, diffusion and rotation, product formation is the first to occur at an appreciable rate as the glass is warmed from -196° .

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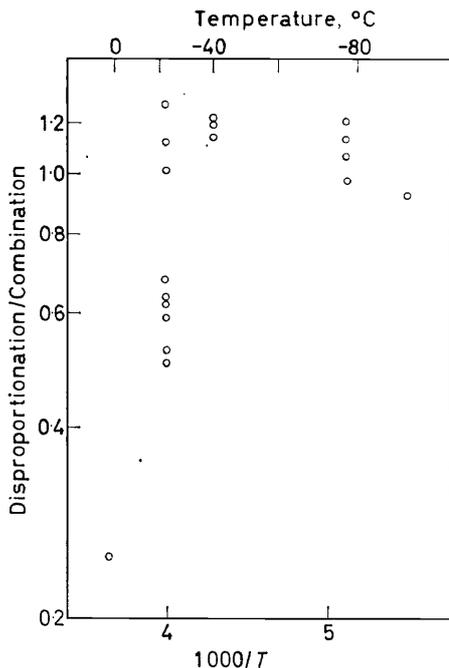


Figure 6. Effect of freezing on the relative amounts of disproportionation and coupling products of *meso*-AMPB (III) in benzene on photolysis.

The fact that the effective rigidities of a series of frozen solutions continue to increase with lowering of the temperature below the freezing point was shown to be a property of the temperature of photolysis and not of the manner of preparation of the frozen solution. The product ratios in a sample frozen rapidly to -70° were the same as those in a sample frozen at -24° and then brought to -70° before the photolysis. Likewise, a solution frozen rapidly to -70° and then raised to -24° showed the ratios characteristic of a solution frozen directly at -24° .

There would appear to be two possible extremes of behaviour during the freezing of a solution. On the one hand, the solvent might separate in pure, uncontaminated crystals surrounded by more and more concentrated solution until at the eutectic point macroscopic crystals of solute are formed interspersed with crystals of solvent. In such a medium one would expect the behaviour of more and more concentrated solutions as the temperature is lowered to the eutectic point where a discontinuity in the environment of the molecules would become pronounced and below which the behaviour would be only that of the crystalline state. Pincock and Kiovsky have recently provided striking examples of this behaviour in the solution phase during such a sequence¹⁶. At the other extreme is the behaviour in glassy solvents in which a lowering of temperature brings about a steady increase in viscosity culminating in a high degree of rigidity but with the solute molecules still separated from one another as in the liquid and surrounded by a tighter solvent cage than any available in the normal liquid state. Our

solutions of benzene and chlorobenzene have a polycrystalline appearance; yet they show the reaction characteristics to be expected of a continuum of steadily increasing viscosity. It appears that either the exclusion of solute from the solvent crystals is incomplete or a glassy state is formed on cooling more rapidly than crystals separate and then when crystals of solvent are formed, it is too late for molecules of the solute to diffuse together to form crystals of their own. In either case, the microscopic viscosity around the isolated solute molecule continues to increase with decreasing temperature even after freezing. This is consistent with the many known cases of transition temperatures in solids associated with rotation of individual molecules which retain their positions relative to their neighbours¹⁷.

Since these frozen solutions give the appearance of a controlled scale of cage effects stretching almost from zero to infinity, it is of interest to analyse the ratios of *meso*/DL and of disproportionation/combination in these terms. Thermolysis and photolysis of AMPB in liquid phase lead to essentially equal amounts of DL and *meso* coupling products. The excess of *meso* over DL in any frozen medium may therefore be taken as a measure of the amount of coupling within the cage. Likewise, the ratios of disproportionation to combination measured in the liquid solution afford a value of $\Delta\Delta H^\ddagger$ from which the disproportionation/combination ratio characteristic of the free radicals in the liquid phase may be calculated for any temperature. *α*-Isopropylstyrene found in excess of this predicted amount in any frozen medium may therefore be presumed to have been formed within the cage.

We can thus deduce for each experiment the fraction of coupling product and the fraction of disproportionation product which have resulted from conditions other than those in solution, i.e. the fractions resulting from rigid cage effects. The ratio of disproportionation to coupling of the free radicals occurring within the cage can be evaluated for each experiment by taking as numerator the excess of *α*-isopropylstyrene over that expected for the freely diffusing radicals and as denominator the excess of *meso*- over DL-TMDPH. A plot of this fraction for all the experiments in frozen benzene is shown in *Figure 7*. All the experiments at -24° show a fairly wide variation in the ratios, which we attribute in part to difficulties of temperature control. The data in *Figure 7*, plotted as the logarithm of the ratio against reciprocal temperature, are compatible with a linear relationship corresponding to an activation energy within the cage which is about 1 kcal higher for disproportionation than for coupling. This difference is in the same direction as in the fluid solutions with the important distinction that the entropy of activation in the cage state favours disproportionation over combination. This effect has been observed also in the behaviour of cumyl radical pairs in frozen media¹⁸. Stuart models support the idea that for a rigidly held pair of 2-phenyl-2,3-dimethyl-2-butyl radicals in contact the transition state for disproportionation should be proportionately easier to attain than that for coupling as compared to a fluid medium.

As a starting material for these experiments *meso*-AMPB was used in most cases because of its availability and purity. However, it was verified that DL-AMPB decomposed in rigid media of this type led, as would be required by our interpretation, to coupling product with substantial excesses of DL-over *meso*-TMDPH.

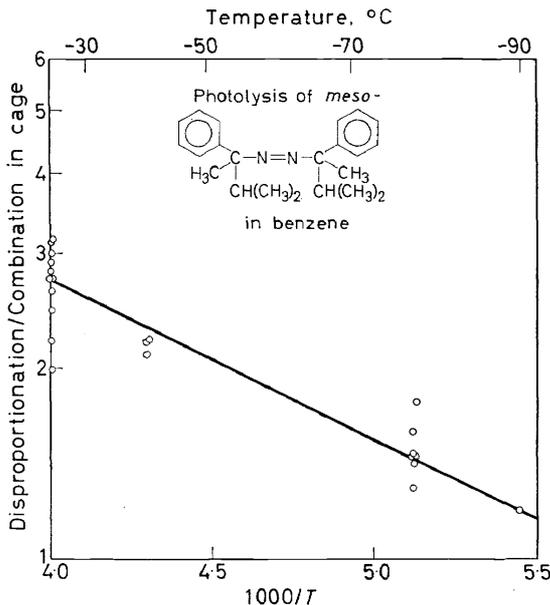


Figure 7. Ratio of that part of disproportionation and combination of radicals occurring in the rigid cage in photolysis of *meso*-AMPB(III) in frozen benzene at different temperatures.

(b) Electron spin resonance observation of triplet radical pairs

As in previous experiments in this laboratory with azo-diphenylmethane, the decomposition of AMPB at 70° or at 0° failed to give any e.s.r. signal of sufficient intensity for definite identification. However, when a degassed 1 M solution of *meso*-AMPB in benzene frozen to a polycrystalline solid at -196° was irradiated with 366 m μ light in the e.s.r. cavity, the signals shown in Figure 8 were obtained. Figure 8b shows the signal at half-field, corresponding to a transition with $\Delta M = 2$, establishing the presence of a triplet state. Figure 8a shows the signal for $\Delta M = 1$ which is some 1000 times more intense than the $\Delta M = 2$ signal. The shape of this signal is consistent with that for randomly oriented triplets with D about 0.011 cm $^{-1}$ and E less than 0.001 cm $^{-1}$ ¹⁹. Its asymmetry is probably due to interference by an unsplit peak which grows with time. After 48 h in the dark at -196° the sample was still bright yellow in the irradiated region and gave an e.s.r. signal (Figure 9a) showing enhancement of the single peak relative to the original signal. After 9 days in the dark at -196° the sample gave the spectrum shown in Figure 9b, very little changed in shape and intensity. At higher temperatures the signal of the triplet state disappeared much more rapidly so that at -150° it was almost completely undetectable 1 h after cessation of irradiation. An almost undetectable steady state concentration of the triplet could be maintained at -35° by continuous irradiation. The unsplit peak persisted to a much higher temperature showing no diminution over 25 min at -125° but disappearing in 15 min at -75°.

E.s.r. signals from randomly oriented triplet states are characteristically

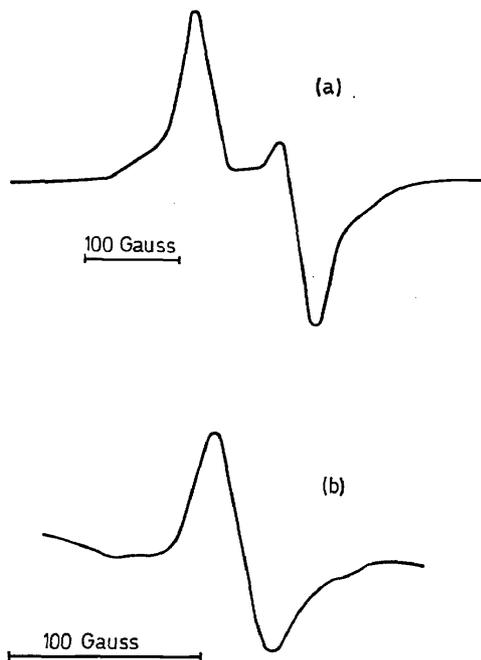


Figure 8. E.s.r. signals of *meso*-AMPB (III) photolyzed at -196° in benzene. (a) $\Delta M = 1$, (b) $\Delta M = 2$.

weak and poorly resolved because of the strong dependence of the signal upon the orientation of the molecule relative to the magnetic field. In an attempt to achieve control of orientation a single needle crystal of AMPB was grown and introduced into the e.s.r. cavity with its needle axis perpendicular to that of the tube. Figure 10 shows the effect of successive 10° rotations upon the spectrum for this sample. The positions of the two doublet signals are plotted as a function of the rotation in Figure 11. Figure 12 shows that an orientation can be defined as "zero rotation" such that the separation of peaks in the e.s.r. spectrum of the single crystal is proportional to the square of the sine of the rotation angle.

This behaviour, diagnostic of the presence of a triplet state, indicates that we are observing either an unprecedented prolonged life of the excited triplet state of an azo compound or a pair of carbon radicals in a cage whose spins interact sufficiently to maintain the existence of a triplet state but which do not combine readily. The separation of the signals can be interpreted in terms of an average separation of the two electrons in the observed triplet state of about $6\text{--}7 \text{ \AA}$,²⁰ if we use the approximation of point dipoles ($D = 0.011 \text{ cm}^{-1} = 3 \beta r^{-3}$). This seems completely incompatible with an excited triplet of an azo compound in which the chromophore is insulated by saturated carbon atoms from the rest of the molecule, and it would seem impossible for the electrons to achieve a greater separation than that of the $\text{N}=\text{N}$ distance. Even the excited triplet of naphthalene²¹ in which the possible interelectronic distance is greater than this gives a triplet signal with a

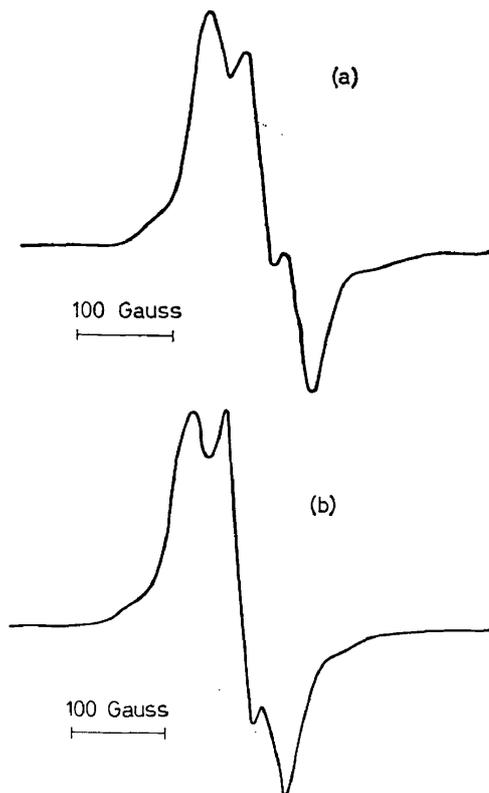


Figure 9. E.s.r. signal from *meso*-AMPB (III) in frozen benzene at -196° , irradiated and then held at liquid nitrogen temperature for (a) 48 h, (b) 9 days.

range about 10 times as broad as ours. The separation indicated would be entirely normal for the delocalized electrons of two hindered radicals held apart in the cage by the non-bonding interactions of the substituent groups, or by a nitrogen molecule which had not yet escaped by diffusion.

DISCUSSION

A number of indications of strong spin coupling in pairs of inorganic radicals have been presented including the coupling between copper atoms in copper acetate²², and that in the various sulphate radical pairs from the photolysis of potassium persulphate²³. There have been several observations of such coupling in organic systems. Thomas, Keller, and McConnell were able to demonstrate²⁴ that in the case of the solid perchlorate salt of Wurster's Blue cation the decrease in magnetic susceptibility of the crystal below 186°K is due to a phase transition during which the equally spaced molecules of spin $\pm 1/2$ shift into pairs with spin ± 1 or spin 0.

In a thorough study of a single crystal of dimethylglyoxime irradiated at -196° , Kurita found the e.s.r. spectrum for a triplet state which he convincingly interpreted as arising from strongly coupled ($D = 0.0144 \text{ cm}^{-1}$)

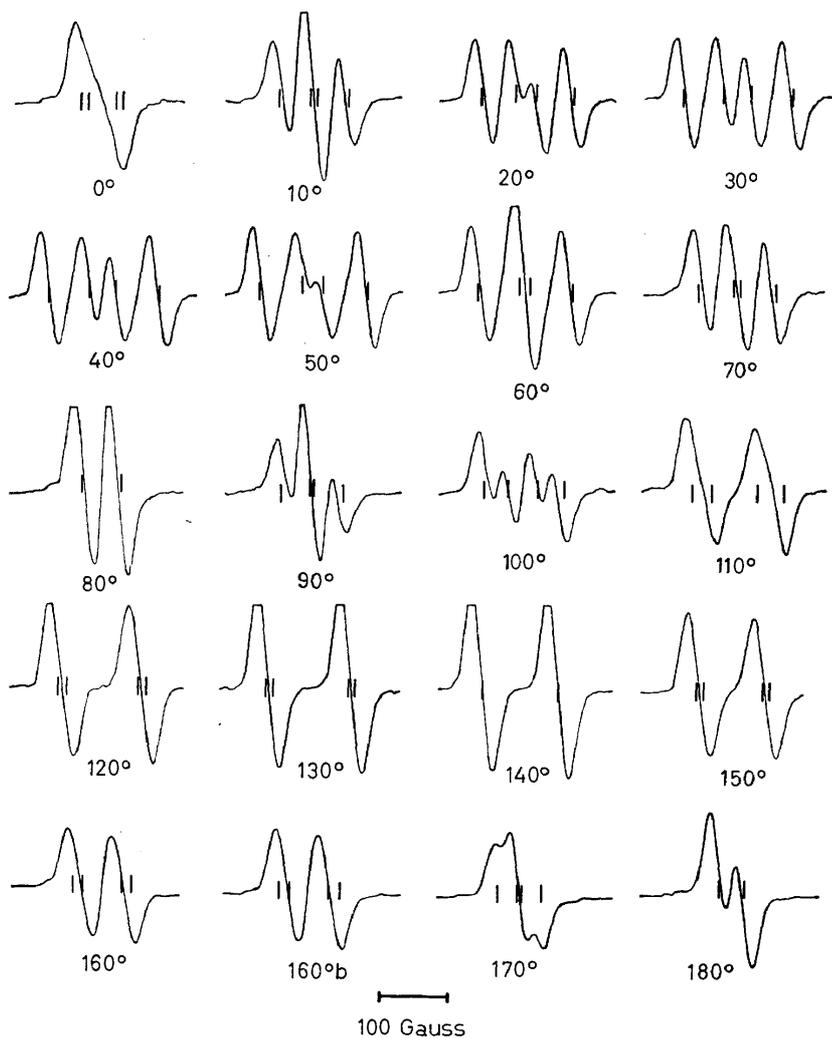


Figure 10. E.s.r. signals from a single crystal of *meso*-AMPB, irradiated at -196° and rotated by 10° increments relative to the magnetic field.

oxy radicals on adjacent molecules in the crystal lattice²⁵. In their study of the electronic interaction in ketyl radicals Hirota and Weissman²⁶ found that numerous alkali metal and alkaline earth ketys existed in part as dimers in which the free spins were strongly coupled to give triplet states with D values ranging from less than 0.0009 cm^{-1} to 0.0152 cm^{-1} . E values for these systems were near zero, perhaps as a result of the large separation of the radical centres. $\Delta M = 2$ transitions were found for all of these cases confirming that the two-spin system has a triplet state.

The triplet radical pair in a solvent cage is a species which has been the goal of several recent researches in this laboratory^{27, 28}. Azocumene and

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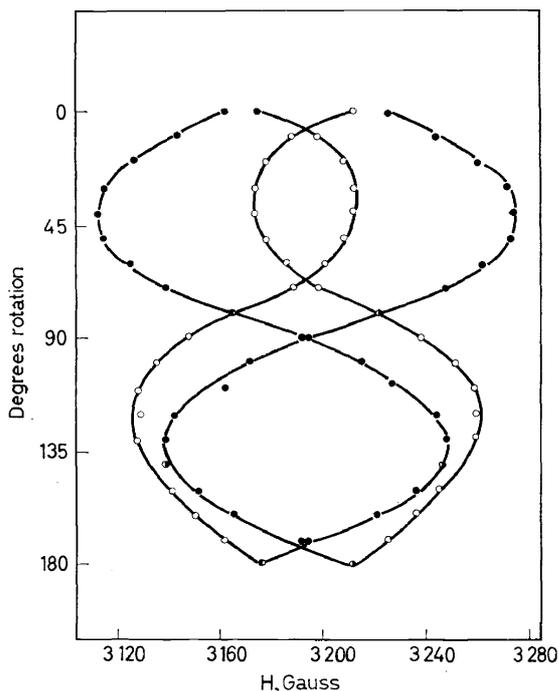


Figure 11. Separation of E.s.r. peaks as a function of angle of rotation of single irradiated *meso*-AMPB crystal relative to magnetic field at -196° .

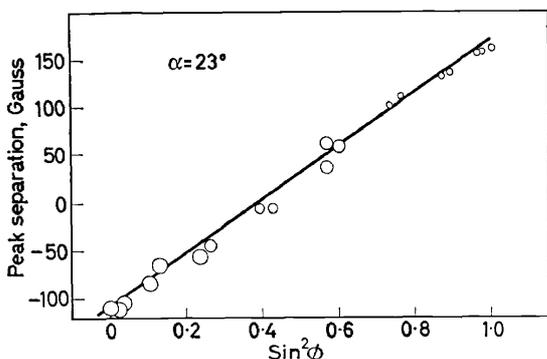


Figure 12. Peak separation in e.s.r. spectrum of irradiated single *meso*-AMPB crystal at -196° , as a function of $\sin^2\phi$

azomethane, which show substantial cage effects when photolyzed or thermolyzed in benzene solution, failed to reveal any different behaviour when the decomposition was carried out by means of a photosensitizer through a triplet precursor as compared to thermal or direct photolytic decomposition. Similar observations have been made with respect to hexafluoroazomethane²⁹ and azobis- α -cyanocyclohexane³⁰. Differing explanations have been offered for these results. Fox and Hammond, who did observe a

result compatible with the expected difference when they photolyzed the related *ketenimine* instead of the azo compound, proposed that the N_2 molecule separating the free radicals after photolysis of the azo compound lowered the triplet-singlet energy gap and likewise reduced their time for interconversion, whereas the lifetime of the triplet radical pair from the *ketenimine* was greater because of the greater interaction of the spins. Nelsen and Bartlett concluded only that spin relaxation of radical pairs from the azo compound must be rapid enough to bring singlet and triplet radical pairs essentially to equilibrium within the time of radical coupling.† Our present demonstration seems to show that triplet radical pairs of the type originally sought do in fact exist at the distance characteristic of radicals emerging from a decomposing azo compound. The persistence of the e.s.r. signals of these radicals over a period of many days might seem at first sight incompatible with the rapid intersystem crossing required by the results of the cage experiments. However, it seems inevitable that in a rigid cage precluding escape of the radicals from each other's vicinity, thermal equilibrium should be established between the singlet and triplet radical pairs. We are thus observing a constantly renewed, dynamic population of triplet pairs in equilibrium with singlet pairs. At low energy separation the triplets will outnumber the singlet pairs 3 to 1; with the triplet state lying above the singlet by 0.1 kcal, the two states will be present in about equal proportions; if the triplet lay above the singlet by 1 kcal, probably much too high at the distance concerned, the triplet population at -196° would be 0.5 per cent of that of the singlet radical pairs. If this is the correct interpretation of our experiments, then the observation of *unpaired* free radicals in a rigid matrix by e.s.r. depends upon one of two circumstances: either the radicals are generated singly, as by electron bombardment, or the rigidity of the medium must be limited enough to allow at least a few radicals to diffuse apart while the rest combine. The triplet radical pair lies on a curve of energy *vs.* separation which becomes more highly repulsive as it approaches the σ -antibonding state of the coupling product; the singlet radical pair lies on the attractive curve, approaching the σ -bonding state, responsible for the rapid and sometimes unactivated coupling of free radicals. At large separations the triplet and singlet radical pairs both become indistinguishable from uncoupled free radicals: the half-field signal of the triplet disappears and the two signals for $\Delta M = 1$ narrow and coalesce. The principal occurrence as the temperature is raised is diffusion of the smallest molecule present, nitrogen, from its position between the radicals, giving rise to rapid coupling and disproportionation. Competing poorly with this is some diffusion apart of the radicals, evidenced by the temporary single-line signals. The

† An ingenious proposal has been made by P. S. Skell (private communication). Since the photosensitizer is presumably present in the same solvent cage with the triplet azo compound and hence with the newly generated triplet radical pair, it is proposed that during the rapid combination of the radicals of the triplet pair the newly deactivated sensitizer is again raised to a triplet state, thus preserving the multiplicity of the total system and utilizing any necessary part of the energy of the newly formed carbon-carbon double bond. This mechanism might, in efficient cases, reveal itself by a quantum yield greater than unity for photosensitized decomposition. It cannot be a general mechanism, for a triplet pair of cumyl radicals could not in coupling to bicumyl release enough energy to raise pyrene or triphenylene to its lowest triplet state.

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hyperfine structure of the 3-methyl-2-phenyl-2-butyl radical, expected to show 48 lines, has not yet been observed.

The experimental details of this work will be published elsewhere³².

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References

- 1 C. Walling. *Free Radicals in Solution*, John Wiley and Sons, Inc., New York, 1957, p. 533, from data of K. Ziegler.
- 2 R. Gomer and G. B. Kistiakowsky. *J. Chem. Phys.* **19**, 85 (1951).
- 3 R. D. Swigert. Thesis, Harvard University, 1964.
- 4 P. D. Bartlett and S. T. Purrington. *J. Am. Chem. Soc.* **88**, 3303 (1966).
- 5 S. F. Nelsen and P. D. Bartlett. *J. Am. Chem. Soc.* **88**, 143 (1966).
- 6 C. H. Bamford and M. J. S. Dewar. *Proc. Roy. Soc. (London)* **A 198**, 252 (1949).
- 7 For example, W. T. Nauta and P. J. Wuis. *Rec. Trav. Chim.* **57**, 41 (1938).
- 8 P. D. Bartlett and T. Funahashi. *J. Am. Chem. Soc.* **84**, 2596 (1962).
- 9 R. J. Crawford, R. J. Dummel, and A. Mishra. *J. Am. Chem. Soc.* **87**, 3023 (1965). Cf. S. Seltzer and F. T. Dunne. *J. Am. Chem. Soc.* **87**, 2628 (1965).
- 10 L. K. Montgomery, K. Schueller, and P. D. Bartlett. *J. Am. Chem. Soc.* **86**, 622 (1964).
- 11 I. V. Berezin. Unpublished work from this laboratory.
- 12 T. E. Stevens. *J. Org. Chem.* **26**, 2531 (1961).
- 13 K. Ziegler. *Angew. Chem.* **61**, 168 (1949).
- 14 L. I. Peterson, Abst. 152nd meeting, American Chemical Society, New York City, September 12-16, 1966, Organic Paper No. 134.
- 15 R. Hiatt and T. G. Traylor. *J. Am. Chem. Soc.* **87**, 3766 (1965).
- 16 R. E. Pincock and T. E. Kiovsky. *J. Am. Chem. Soc.* **87**, 2072, 4100 (1965).
- 17 C. P. Smyth. *Dielectric Behavior and Structure*, McGraw-Hill, New York, 1955, Chapter 5.
- 18 S. F. Nelsen and P. D. Bartlett. *J. Am. Chem. Soc.* **88**, 1397 (1966).
- 19 E. Wasserman, L. C. Snyder, and W. A. Yager. *J. Chem. Phys.* **41**, 1763 (1964).
- 20 N. Hirota and S. I. Weissman. *J. Am. Chem. Soc.* **86**, 2538 (1964); Y. Kurita. *J. Chem. Phys.* **41**, 3926 (1964).
- 21 C. A. Hutchison, Jr., and B. W. Mangum. *J. Chem. Phys.* **29**, 952 (1958). For a table of *D* values of some triplet molecules of a range of sizes, see M. Bersohn and J. C. Baird, *An Introduction to Electron Paramagnetic Resonance*, W. A. Benjamin, New York, 1966, Table 8-1, p. 121.
- 22 B. Bleaney and K. D. Bowers. *Proc. Roy. Soc. (London)* **A 214**, 451 (1952).
- 23 P. W. Atkins, M. C. R. Symons, and P. A. Trevalion. *Proc. Chem. Soc.* **222** (1963).
- 24 D. D. Thomas, H. Keller, and H. M. McConnell. *J. Chem. Phys.* **39**, 2321 (1963).
- 25 Y. Kurita. *J. Chem. Phys.* **41**, 3926 (1964).
- 26 N. Hirota and S. I. Weissman. *J. Am. Chem. Soc.* **86**, 2538 (1964).
- 27 S. F. Nelsen and P. D. Bartlett. *J. Am. Chem. Soc.* **88**, 143 (1966).
- 28 P. Engel, unpublished work.
- 29 M. Szwarc, private communication.
- 30 J. R. Fox and G. S. Hammond. *J. Am. Chem. Soc.* **86**, 4031 (1964).
- 31 S. Kodama. *Bull. Chem. Soc. Japan.* **35**, 824 (1962).
- 32 see J. M. McBride. Thesis, Harvard University, 1966.