Organic Anions. Part 2.[1a] Spectroscopic Studies of 1,3-Diarylpropenide Ions [1b]

By **Richard J. Bushby** * and **Gerald J. Ferber**, Department of Organic Chemistry, The University, Leeds LS2 9JT

Electronic absorption, ^1H n.m.r., and ^{13}C n.m.r. spectra have been determined for eight sodium (and in some cases lithium and potassium) 1,3-diarylpropenides (I) in liquid ammonia. These show that, in this medium, contact ion pairs are not formed and that not only the *trans,trans*-anions (I) but also small amounts of the *cis,trans*-anions (II) are present. The rate of interconversion of the *trans,trans*- and *cis,trans*-forms is too low to be measured by n.m.r. spectroscopy but from the proton-decoupled ^{13}C n.m.r. spectra of the unsubstituted diphenylpropenide (IIIa) it is possible to measure the rate of rotation of the phenyl group. The barrier to this rotation, $\Delta G^{\ddagger}_{rot} = 10.9$ kcal mol^{-1}, is essentially independent of the nature of the counter-ion (Li^+, Na^+, or K^+).

LIKE the equilibration studies described in the last paper, the spectroscopic work described here was initially undertaken in order to provide necessary background information for the ambident reactivity work described in Part 3.[2] In particular it was hoped to provide information on the ion pairing behaviour of diarylpropenide ions (I) in liquid ammonia and on the effect of different substituents X on the charges at the allylic sites ' a ' and ' b '.

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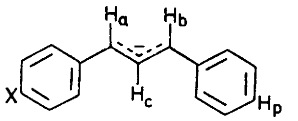
[1] (*a*) Part 1, R. J. Bushby and G. J. Ferber, preceding paper; (*b*) preliminary communication, R. J. Bushby and G. J. Ferber, *Tetrahedron Letters*, 1974, 3701.

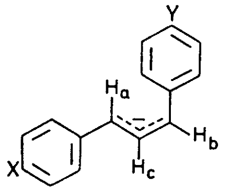
[2] Part 3, R. J. Bushby and G. J. Ferber, following paper.

Although recent studies have greatly clarified our understanding of the allyl-lithium contact ion pair [3] we still do not know how its structure is affected by unsymmetrical substitution of the allyl moiety. Presumably the counter-ion is no longer symmetrically placed and this, in turn, must exert a preferential influence on the reactivity of one or the other of the allylic sites. Until this structural problem is solved interpretation of the ambident reactivity of contact ion pairs, or indeed higher aggregates,[4] is likely to remain an insoluble problem. For the ambident reactivity work it was, therefore, important to establish that the sodium 1,3-diarylpropenides in liquid ammonia did not form contact ion pairs or aggregates. In achieving this end it was possible to draw a number of parallels to the detailed studies by Burley and Young [5-9] of the ion pairing behaviour of the anions (III) and (IV) in ether solvents.

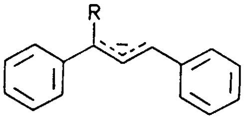
(I)



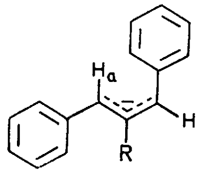
(II)



(III) a; R=H
b; R=alkyl



(IV)



The other aim of these studies, which was also related to the ambident reactivity problem, was to use the n.m.r. spectra of the anions (I) to measure the charge difference between the benzylic sites. The idea of a charge–n.m.r. chemical shift relationship dates back to the work published by Fraenkel in 1960 [10] and has been used, sometimes in a rather uncritical manner, by many other workers. In a recent review Farnum [11] once again stresses that other factors besides charge (*e.g.* neighbouring group bond anisotropies, ring currents, hybridisation, *etc.*) influence chemical shift and must sometimes be taken into account. For the present systems, however, except for the difference in local charge, the environments of the benzylic sites are virtually identical, and so it was hoped that in this case there would be a simple, linear charge–chemical shift relationship. This hope was strengthened *a priori* by the fact that the charges are negative and fairly small and *a posteriori* by the close correlation between the charge difference as measured by ^{1}H n.m.r. and by ^{13}C n.m.r. spectroscopy.[11]

Electronic Absorption Spectra.—Burley and Young have shown that in ether solvents the solvent-separated ion pairs of the anions (IIIa) and (IIIb) give rise to a single absorption $\lambda_{max.}$ 561—569 nm and the contact ion pairs to one or two peaks between 445 and 537 nm.[5-7] As expected,[12] the position of the peak corresponding to the solvent-separated ion pair is fairly independent of the nature of the counter-ion and is close to the position for the free anion. The position of the absorption maximum for the contact ion pair is, however, strongly counter-ion dependent. As may be seen from Figure 1, the behaviour of 1,3-diphenylpropenide ion in liquid ammonia is rather different. Two absorptions are

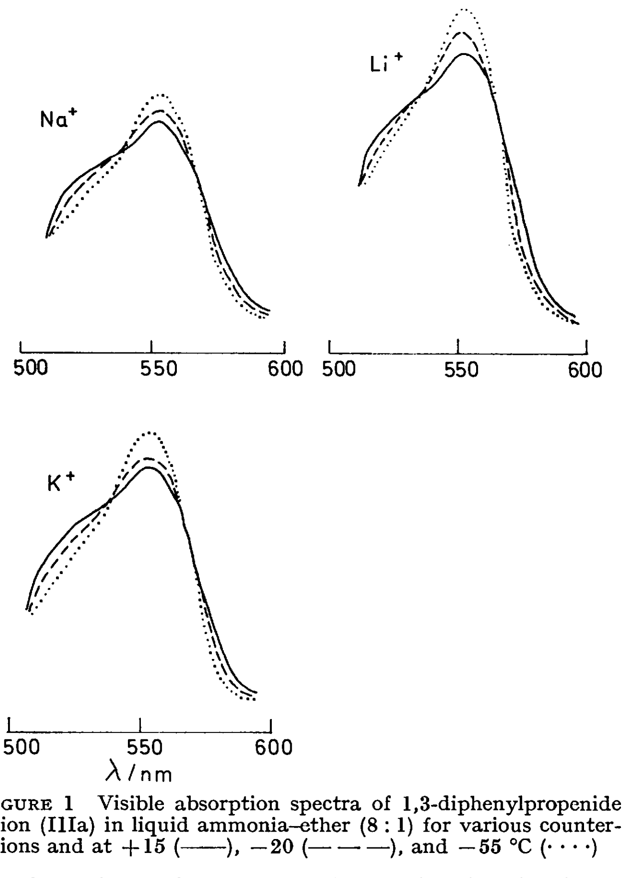


FIGURE 1 Visible absorption spectra of 1,3-diphenylpropenide ion (IIIa) in liquid ammonia–ether (8 : 1) for various counter-ions and at +15 (——), −20 (— — —), and −55 °C (· · · ·)

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[3] P. A. Scherr, R. J. Hogan, and J. P. Oliver, *J. Amer. Chem. Soc.*, 1974, **96**, 6055; J. F. Sebastian, J. R. Grunwell, and B. Hsu, *J. Organometallic Chem.*, 1974, **78**, C1; E. R. Tidwell and B. R. Russell, *ibid.*, 1974, **80**, 175.

[4] P. West, J. I. Purmort, and S. V. McKinley, *J. Amer. Chem. Soc.*, 1968, **90**, 797; P. West, R. Waack, and J. I. Purmort, *ibid.*, 1970, **92**, 840.

[5] J. W. Burley and R. N. Young, *Chem. Comm.*, 1969, 1127.

[6] J. W. Burley and R. N. Young, *J. Chem. Soc.* (*B*), 1971, 1018.

[7] J. W. Burley and R. N. Young, *J.C.S. Perkin II*, 1972, 835.

[8] J. W. Burley and R. N. Young, *J.C.S. Perkin II*, 1972, 1006.

[9] J. W. Burley and R. N. Young, *J.C.S. Perkin II*, 1972, 1843.

[10] G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, 1960, **82**, 5846.

[11] D. G. Farnum, *Adv. Phys. Org. Chem.*, 1975, **11**, 123.

[12] 'Ions and Ion Pairs in Organic Reactions,' ed. M. Szwarc, Wiley–Interscience, vol. I, 1972.

observed, $\lambda_{\max.}$ 550 and 525 nm. Variable temperature studies (*i.e.* the occurrence of an isosbestic point) are consistent with the assignment of these absorptions to two distinct species which exist as a rapidly equilibrating pair and further that the more stable form is associated with the peak at longer wavelength. The position and relative intensities of these peaks are independent of counter-ion (Li^+, Na^+, or K^+) and also dilution (up to five-fold) suggesting that both must be due to solvent-separated ion pairs or possibly free ions.[13] The peak $\lambda_{\max.}$ 550 nm is assigned to the *trans,trans*-1,3-diphenylpropenide ion (IIIa). The hypsochromic shift experienced in passing from ether solvents to ammonia is not wholly unexpected.[14,15] It is similar in magnitude to the hypsochromic shift recorded for the solvent-separated ion pair of fluorenide ion (ethers $\lambda_{\max.}$ 372—374 nm; ammonia [15] $\lambda_{\max.}$ 365 nm) and presumably it has a similar explanation.[16] The peak $\lambda_{\max.}$ 525 nm is more tentatively assigned to the *cis,trans*-1,3-diphenylpropenide ion (IV; R = H). Independent evidence for the occurrence of small amounts of this species in solution from ^{1}H n.m.r. and from acid-quenching studies [2] will be described later. Furthermore Burley and Young showed that, whereas the solvent-separated ion pairs of the *trans,trans*-anions (IIIa and b) in ether solvents gave rise to an absorption maximum at 561—569 nm,[5-7] the solvent-separated ion pair for the *cis,trans*-anion (IV; R = Me) [9] under similar conditions gave rise to an absorption maximum $\lambda_{\max.}$ 536 nm. The hypsochromic shift is similar in magnitude to that in the present case and models show that it possibly arises from non-planarity of the phenyl rings in the *cis,trans*-form. The *para*-substituted anions (I; X $\neq$ H) all have spectra which are very similar to that of the parent anion. In the *meta*-fluoro-substituted system, however, only a single smooth peak was observed, $\lambda_{\max.}$ 544 nm, the shape of which was little affected by variation of temperature (−55 to +15 °C). In this system, however, as well as the normal possibility of *cis–trans*-isomerism there are several possible rotamers involving the substituted phenyl ring, and presumably the observed absorption is a complex envelope due to several of these species. Substitution of the aromatic ring has remarkably little effect on the positions of the absorption maxima. This is consistent with the similarity between the electronic absorption spectra of (IIIa) and (IIIb) noted by Burley and Young [7] and also the results of Astaf'ev and Shatenshtein for the potassium salts of *para,para'*-disubstituted diphenylmethanes in liquid ammonia.[17]

TABLE 1

^{1}H N.m.r. spectra for 0.5M-solutions of *trans,trans*-1,3-diarylpropenide ions in 15% methyl t-butyl ether–85% liquid ammonia

X	Counter-ion	Temp. (°C)	δ_X [b]	δ_c [b]	δ *ortho* and *meta* [b]	δ_p [b]	δ_a [a]	δ_b [a]	$\delta_b - \delta_a$ [a]	J_{ac}/Hz [a]	J_{bc}/Hz [a]
p-Me_2N	Na^+	−30	2.65 [d]	7.18	6.3—6.8	5.77	4.74	4.55	−0.19	13.4	12.4
p-Me_2N	Li^+	−30	2.63 [d]	7.17	6.3—6.8	5.77	4.75	4.55	−0.20	13.5	12.9
p-MeO	Na^+	−30	3.60	7.17	6.3—6.8	5.79	4.73	4.56	−0.17	13.5	12.6
p-Bu^t	Na^+	0	*c*	7.29	6.5—6.9	5.90	4.76	4.67	−0.09	13.8	13.3
p-Me	Na^+	−30	2.02	7.27	6.4—6.8	5.87	4.72	4.62	−0.10	13.0	12.9
p-Me	Li^+	−12	2.02	7.26	6.4—6.8	5.90	4.74	4.64	−0.10	13.1	13.1
H	Na^+	−30		7.31	6.4—6.8	5.96	4.71	4.71	0.00	12.9	12.9
p-F	Na^+	−30		7.22	6.4—6.9	5.93	4.70	4.66	−0.04	12.8	12.7
p-Cl	Na^+	0		7.24	6.4—6.9	6.08	4.66	4.80	+0.14	12.6	13.4
m-F	Na^+	+10		7.29	6.4—6.9	6.20 [e]	4.70 [f]	4.84	+0.14	12.1	13.1

[a] Sweep width 10 Hz cm^{-1}. [b] Sweep width 4 Hz cm^{-1}. [c] Hidden by solvent resonances. [d] Additional signal *ca.* 8% of the main resonance *ca.* 0.06 p.p.m. downfield. [e] δ_p (substituted ring) 5.55. [f] J_{HF} 1.9 Hz.

^{1}H *N.m.r. Spectra.*—Although generally less reliable than electronic absorption spectroscopy, ^{1}H n.m.r. spectroscopy can also be used to study the nature of ion pairs in solution. Burley and Young have shown that, for the solvent-separated ion pairs of the anions (IIIa and b) in ether solvents, the chemical shifts of the benzylic protons are only weakly dependent on the counter-ion whereas for the contact ion pairs a stronger dependence on the nature of the counter-ion is observed. Comparison of the ^{1}H n.m.r. spectra of sodium and lithium salts of the methyl and dimethylamino-substituted anions (I; X = Me and Me_2N) in liquid ammonia (Table 1) again suggests that solvent-separated ion pairs are present.

This Table also summarises the ^{1}H n.m.r. spectra for all the anions studied. The t-butyl resonance of methyl t-butyl ether was used as internal lock and standard but the chemical shifts are quoted relative to Me_4Si. In all cases 0.5M-solutions were used and in most cases the spectrum was recorded at −30 °C, although it was shown that neither temperature (+10 to −30 °C) [8] nor concentration (0.25—1.0M) significantly affected the chemical shifts, and in some cases higher temperatures were

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[13] Typically, dissociation constants for monoelectrolytes in liquid ammonia, as derived by conductivity studies, are *ca.* 10^{-3} mol l^{-1} at *ca.* −40 °C (V. F. Hnizda and C. A. Kraus, *J. Amer. Chem. Soc.*, 1949, **71**, 1565; R. E. Cuthrell, E. C. Fohn, and J. J. Lagowski, *Inorg. Chem.*, 1966, **5**, 111; J. B. Gill and B. M. Lowe, *J.C.S. Dalton*, 1972, 1959). Electronic absorption spectroscopy was carried out at a concentration between *ca.* 1×10^{-5} and 5×10^{-5} mol l^{-1} and it seems possible that at this concentration free ions are the predominant species present. The n.m.r. studies were, however, performed in 0.5M-solutions and in this case solvent-separated ion pairs must predominate. At this concentration, and certainly at concentrations much in excess of this, however, a simple count of the number of solvent molecules available shows that the distinction between ' free ' ions and solvent-separated ion pairs becomes virtually meaningless.

[14] C. Pillot, J.-P. Pascault, and J. Golé, *Bull. Soc. chim. France*, 1974, 357.

[15] J.-P. Pascault and J. Golé, *J. Chim. phys.*, 1971, **68**, 442.

[16] J.-P. Pascault and J. Golé, *J. Chim. phys.*, 1971, **68**, 453; *Bull. Soc. chim. France*, 1974, 362.

[17] I. V. Astaf'ev and A. I. Shatenshtein, *Optics and Spectroscopy*, 1959, **6**, 410.

preferred as the resolution at −30 °C was rather poor. The assignment of signals for the parent anion (I; X = H) is straightforward and in agreement with that reported by other workers.[8,18,19] In this anion the benzylic sites ' a ' and ' b ' are equivalent and give rise to a doublet, δ 4.71. In other cases, X ≠ H, the benzylic sites are non-equivalent and, as expected, a pair of doublets is observed in this region of the spectrum. A semiquantitative picture of the effect of substituents on the charge distribution, and hence on the chemical shifts of protons ' a ' and ' b ', can be obtained from HMO calculations.[20] These show that an electron-donating substituent ' X ' in the *para*-position should result in slight deshielding of proton ' a ' and strong shielding of proton ' b ' and that an electron-withdrawing substituent ' X ' in the *meta*- or *para*-position should slightly shield proton ' a ' and more strongly deshield proton ' b '. This enables most of the signals for the benzylic protons to be assigned without difficulty and the general pattern is confirmed by the spin splitting observed between fluorine and H_a in the *meta*-fluoro-substituted anion. The only difficulty was the *para*-fluoro-substituted anion (I; X = F) where, as expected, the perturbation caused by the fluorine was very small. As *para*-fluorine can act either as a weak electron-withdrawing or as an electron-donating substituent[21] this made assignment of the benzylic signals difficult and so an anion was prepared which was 21% enriched with ^{13}C at position ' b '. The signals for the benzylic protons could then be assigned from the position of the ^{13}C satellites. The ^1H, ^{13}C one-bond coupling constant obtained for this compound was 145.8 Hz, close to the value expected for sp^2-hybridised carbon.[22] Moderately good linear correlations are obtained between the substituent constant σ and the chemical shifts of H_a(r = 0.697; 8 points) and H_b (r = 0.872) and also the difference ($\delta_b - \delta_a$) (r = 0.886). Of more practical significance is the linear correlation (r = 0.986) between the chemical shifts of H_b and the corresponding *para*-proton, H_p, a finding which lends support to those workers who have used the chemical shifts of *para*-protons as an index of the charge at corresponding benzylic positions.[23]

Although the ^1H n.m.r. spectrum of 1,3-diphenylpropenide ion has been separately reported by three sets of workers[8,18,19] they have only recorded the signals for the *trans,trans*-conformation (I; X = H). It was, therefore, rather surprising to find that a set of weaker signals could be detected which were attributable to the benzylic hydrogens of the *cis,trans*-conformation (II; X = Y = H). As may be seen from Table 2 the positions of these signals were close to those reported for the benzylic hydrogens of the potassium salt of the anion (IV; R = Me) which is known to adopt a *cis,trans*-conformation.[9] Accurate integration of small n.m.r. signals is difficult but suggests that in 15% methyl t-butyl ether–85% ammonia at −30 °C the parent system gives an equilibrium mixture of *ca.* 93% *trans,trans*-(I; X = H) and *ca.* 7% *cis,trans*-(II; X = Y = H) conformer. In the unsymmetrically substituted systems, X ≠ H, two *cis,trans*-conformers must be considered and the splitting of the n.m.r. signals together with their low intensity means that for 0.5M-solutions the signal-to-noise ratio was too low and definite assignments could not be made. However, for the *para*-fluoro-substituted anion an n.m.r. spectrum was determined on a 1M-solution and in this case the signals due to the *cis,trans*-conformers could be clearly observed. They showed that at +10 °C the *cis,trans*-anions (II; X = F, Y = H; X = H, Y = F) account for *ca.* 10% of the total anion present. It is also noteworthy that for the dimethylamino-substituted system (I; X = Me_2N) two *N*-methyl resonances were observed (Table 1; 8%, δ 2.71; 92%, δ 2.65). Although the weaker of these two signals cannot be definitely assigned it seems at least possible that it is due to one or both of the *cis,trans*-conformers.

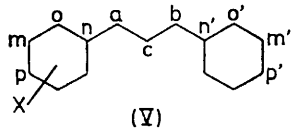
TABLE 2

^1H N.m.r. data for *cis,trans*-anions

Anion	Counter-ion	Temp. (°C)	δ_a	δ_b	J_{ac}/Hz	J_{bc}/Hz
(II; X = H)[a]	Na^+	−30	5.23	4.28	13.8	10.2
(II; X = F, Y = H;	Na^+	+10	5.18	4.25	14.6	10.6
X = H, Y = F)[a]			5.23	4.29	14.6	11.2
(IV; R = Me)[9,c]	K^+	−35	5.23[b]	4.10[b]		

[a] 15% methyl t-butyl ether–85% ammonia. [b] In the original paper[9] these are assigned the opposite way round but a simple consideration of ring current effects shows this to be incorrect. [c] Tetrahydrofuran.

^{13}C *N.m.r. Spectra.*—^{13}C N.m.r. chemical shifts for the 1,3-diarylpropenide ions (I) are summarised in Table 3. The conditions used were very similar to those employed in determining the ^1H n.m.r. spectra. The assignment of signals for the parent anion (V; X = H) (Figure 2) is fairly straightforward and follows that made by other workers for related systems.[22] The only problem is the position of the signal for the centre carbon of the allylic system ' c ' (? δ 129.0) which appears to overlap with that for the *meta*-carbons (δ 128.8). For the unsymmetrically substituted anions the aromatic carbon signals can be assigned by using normal aromatic chemical shift parameters[24] and in the fluoro-substituted systems some of



(V)

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[18] G. J. Heiszwolf and H. Kloosterziel, *Rec. Trav. chim.*, 1967, **86**, 1345.

[19] H. H. Freedman, V. R. Sandel, and B. P. Thill, *J. Amer. Chem. Soc.*, 1967, **89**, 1762.

[20] This should be compared with HMO calculations on other substituted allyl and pentadienyl anion: G. J. Hoijtink and J. van Schooten, *Rec. Trav. chim.*, 1953, **72**, 691; N. Bouman and G. J. Hoijtink, *ibid.*, 1957, **76**, 841; H.-U. Wagner and H. H. Vogt, *Tetrahedron Letters*, 1974, 775.

[21] P. Politzer and J. W. Timberlake, *J. Org. Chem.*, 1972, **37**, 3557.

[22] J. P. C. M. van Dongen, H. W. D. van Dijkman, and M. J. A. de Bie, *Rec. Trav. chim.*, 1974, **93**, 29.

[23] R. F. Hudrlik and R. C. Dabrowski, *Tetrahedron Letters*, 1973, 3731; H. O. House, R. A. Auerbach, M. Gall, and N. J. Peet, *J. Org. Chem.*, 1973, **38**, 575.

[24] J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972, ch. 5.

these can be confirmed from the magnitudes of the C,F-coupling constants. Most of the benzylic carbon signals can be assigned by using the same arguments as those employed for the benzylic protons. However, for the *para*-fluoro-substituted system the chemical shifts of the two benzylic carbons are very similar and, to make a definite assignment, an anion was prepared 3% enriched with ^{13}C at carbon atom ' b '. Moderately good linear correlations are obtained between the substituent constant σ and the chemical shifts of C_a ($r = 0.755$; 8 points) and C_b ($r = 0.878$) and also the difference ($\delta_b - \delta_a$) ($r = 0.916$). Of more significance for the ambident reactivity studies described in Part 3 is the linearity of the plot of ^1H benzylic *versus* ^{13}C benzylic chemical shift ($r = 0.965$; 15 points) and more especially the plot of ($\delta_b - \delta_a$) for the ^1H and ^{13}C results ($r = 0.989$; 8 points). The slope of this latter graph (22.5) presumably reflects the difference in sensitivity of ^{13}C and ^1H chemical shifts to local charge.[11] The signal-to-noise ratio obtained for the ^{13}C spectra was inferior to that obtained for the ^1H spectra and none of the few ' spurious ' minor peaks observed could be assigned with any certainty to the *cis,trans*-anion.

TABLE 3

^{13}C N.m.r. data for 0.5M solutions of sodium *trans,trans*-1,3-diarylpropenides in 15% [$^2H_3$]methyl t-butyl ether–85% liquid ammonia at −10 °C

X	δ_n	δ_n'	δ_o and δ_o'	δ_m	δ_m'	δ_p	δ_p'	δ_a (±0.07)	δ_b (±0.07)	$\delta_b - \delta_a$ (±0.14)	δ_X
para-Me_2N	139.3	147.1	118, 119.7	117.3	128.9	142.0	109.2	90.84	86.81	−4.03	43.1
para-MeO	141.0	147.3	118, 119.3	115.1	128.9	150.3	109.8	90.06	87.14	−2.92	55.8
para-Bu^t	144.5	147.1	117, 118.6	125.4	128.9	134.7	110.9	90.39	88.63	−1.76	31.9, 33.7 [a]
para-Me	144.3	147.0	118, 118.8	129.4 [b]	128.8 [b]	121.1	110.8	90.45	88.44	−2.01	20.8
H	146.9	146.9	118.5, 118.5	128.9	128.9	112.1	112.1	90.30	90.30	0.00	
para-F	144.0	147.1	118.1,[c] 118	115.3 [d]	128.9	?	111.5	88.83	89.22	0.39	
para-Cl	145.5	146.2	119, 119.2	128.4 [b]	128.9 [b]	?	113.6	89.09	92.47	3.38	
meta-F	?	146.4	119,5. ?	129.7 [e]	128.9	95.9 [f]	114.2	89.54	93.19	3.65	

[a] Quaternary carbon. [b] These signals, due to *meta*-carbons, could not be assigned with certainty. [c] J_{CF} 5.9 Hz. [d] J_{CF} 20.6 Hz. [e] J_{CF} 2.3 Hz. [f] J_{CF} 22.1 Hz.

Figure 2 shows that the signal due to the *ortho*-carbons (δ 118.5) of *trans,trans*-1,3-diphenylpropenide ion at −10 °C is significantly broadened, and it was found that as the temperature was lowered the signal broadened still further and eventually split into two peaks (δ 115.4 and 121.3). This reflects ' freezing out ' of the rotation of the phenyl groups. The coalescence temperature was *ca.* −40 °C and corresponds to an energy barrier, $\Delta G^{\ddagger}_{rot} = 10.9$ kcal mol^{-1}. By computer-aided matching of observed and calculated lineshapes [25] it was possible to measure the rates of rotation for the phenyl groups of the lithium, sodium, and potassium salts at several different temperatures between −37.5 and 61.1 °C; the results are summarised in Table 4. Differences between the rates for the different counter-ions are small and probably within experimental error. This confirms that solvent-separated ion pairs are present in solution and shows that, unlike many other group 1 organometallic compounds, rotation itself does not involve a change in ion-pair type.[26-28] It was also shown that the rate of rotation was independent of the concentration of amide ion in excess (up to 30%), eliminating the possibility of a protonation–deprotonation mechanism.[29] An Arrhenius plot based on the data in Table 4 yields the parameters $\log_{10} A = 11.46 \pm 0.63$ and $E_a = 9.60 \pm 0.65$ kcal mol^{-1}.

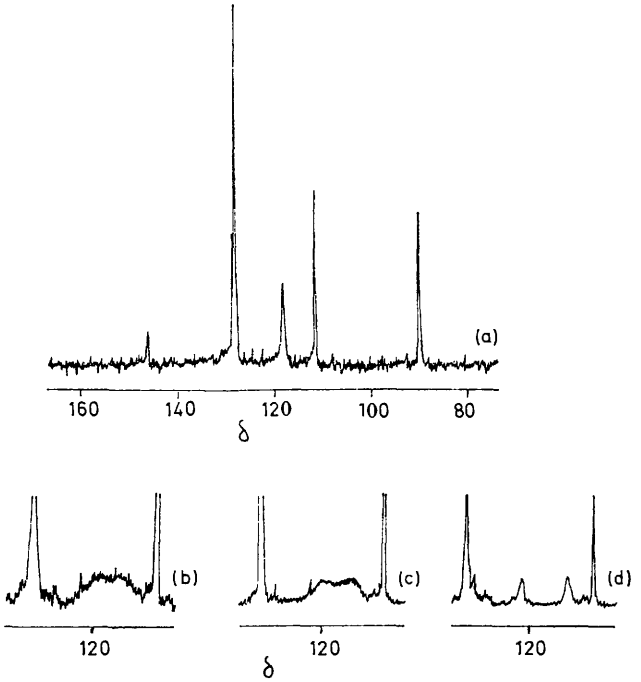

FIGURE 2 Proton-decoupled ^{13}C n.m.r. spectrum of 1,3-diphenylpropenide ion in 15 % [$^2H_3$]methyl t-butyl ether–85% liquid ammonia: (a) Na^+ salt at −10 °C; (b) Li^+ salt at −42.7 °C; (c) K^+ salt at −42.2 °C; (d) Na^+ salt at −57.6 °C

The energy barrier to phenyl rotation is close to that in phenyl-substituted ketones and aldehydes [30] and it is

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[25] The computer program was based on the outline given in B. G. Cox, F. G. Riddell, and D. A. R. Williams, *J. Chem. Soc.* (*B*), 1970, 859.

[26] R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Letters*, 1967, 205.

[27] F. J. Kronzer and V. R. Sandel, *J. Amer. Chem. Soc.*, 1972, **94**, 5750.

[28] G. Fraenkel, J. G. Russell, and Y.-H. Chen, *J. Amer. Chem. Soc.*, 1973, **95**, 3208.

[29] G. J. Heiszwolf, J. A. A. van Drunen, and H. Kloosterziel, *Rec. Trav. chim.*, 1969, **88**, 1377.

[30] F. A. L. Anet and M. Ahmad, *J. Amer. Chem. Soc.*, 1964, **86**, 119; R. E. Klinck, D. H. Marr, and J. B. Stothers, *Chem. Comm.*, 1967, 409; N. Nakamura and M. Oki, *Bull. Chem. Soc. Japan*, 1972, **45**, 2565.

interesting to compare it with barriers for rotation in other group 1 organometallics.

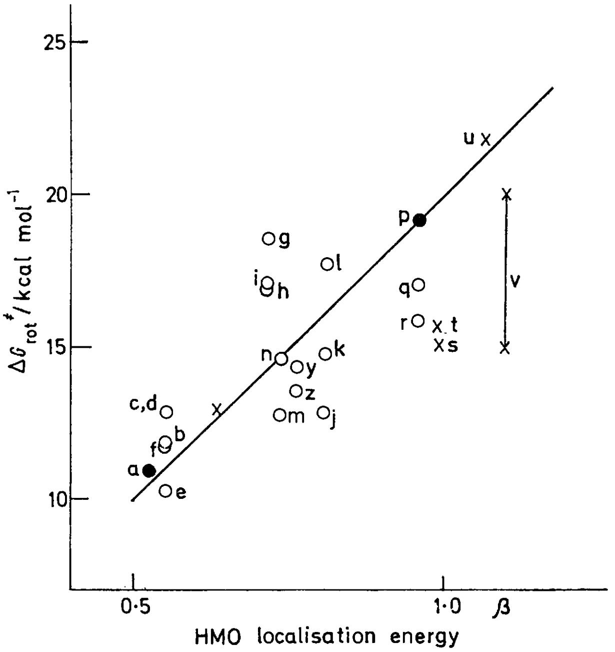

FIGURE 3 Energy barriers for internal rotation in group 1 organometallics. ' Theoretical line ' is based on barriers of 0 for ethane and 40 for ethylene.

a	C_6H_5–O–$\bar{C}$H–CH=CH–C_6H_5, Li^+, Na^+, and K^+ salts in 15% [$^2H_3$]methyl t-butyl ether–85% liquid ammonia at −40 °C; present work
b—f	C_6H_5–O–$\bar{C}$H–CH=CH_2, respectively the Li^+, Na^+, and K^+ salts in tetrahydrofuran and Li^+ and Na^+ salts in ether all at −15 °C; V. R. Sandel, S. V. McKinley, and H. H. Freedman, *J. Amer. Chem. Soc.*, 1968, **90**, 495
g—i	C_6H_5–O–$\bar{C}$MeCH_2·CMe_3, *p*-$Bu^tC_6H_4$— $\bar{C}$MeCH_2·CMe_3, and *p*-$Pr^iC_6H_4$— –$\bar{C}$MeCH_2·CMe_3, Li^+ salts in tetramethylethylenediamine–iso-octane at 25 °C; ref. 28
j—l	α-Nap–O–$\bar{C}H_2$, Li^+, Na^+, and K^+ salts in tetrahydrofuran at 25 °C (Nap = naphthyl); ref. 27
m, n	β-Nap–O–$\bar{C}H_2$, Li^+, and Na^+ salts in tetrahydrofuran at 25 °C; ref. 27
p	Me$\bar{C}$H–O–CH=CH–C_6H_5, K^+ salt in ammonia at −20 °C; ref. 29
q, r	$\bar{C}H_2$–O–CH=CH–C_6H_5, Li^+ salt in tetrahydrofuran and ether at 55 °C; ref. as for b—f
s	$\bar{C}H_2$–O–CH=CH–CH=CH_2, Li^+ salt in tetrahydrofuran at 30 °C; ref. 26
t	Me$\bar{C}$H–O–CH=CH–CH=CH_2, K^+ salt in ammonia at −50 °C; H. Kloosterziel and J. A. A. van Drunen, *Rec. Trav. chim.*, 1970, **89**, 270.
u	Me$\bar{C}$H–O–CH=CH–CH=CH–CH=CH_2, K^+ salt in ammonia at 0 °C; ref. as for t
v	$\bar{C}H_2$–O–CH=C$(CH=CH_2)_2$ and substituted forms, Li^+ salts in tetrahydrofuran; R. B. Bates, S. Brenner, and C. M. Cole, *J. Amer. Chem. Soc.*, 1972, **94**, 2130
w	CH_2=CH–O–$\bar{C}$H–CH=CH_2, Li^+ salt in tetrahydrofuran at −5 °C; ref. 26.
y, z	C_6H_5–$\bar{C}$H–O–CMe=CH–C_6H_5, Li^+ and K^+ salts in tetrahydrofuran at 30 and 15 °C; ref 9

Figure **3** shows a plot of these energy barriers against the corresponding HMO localisation energies. Systems for which it seems likely that free ions or solvent-separated ion pairs are present and for which there is no change in ion pair type during rotation are indicated by filled circles. (Despite the reservations expressed by Kronzer and Sandel[27] this is taken to include the results of Kloosterziel[29] on the phenylallyl systems.) Although the data are limited, and agreement may be fortuitous, it is interesting that these points lie close to the theoretical line. Systems for which it is not possible to say what sort of ion or ion pair is involved are indicated by a cross. Systems for which the rate of rotation is counter-ion dependent (indicating that, at least, *for some of the counter-ions*, ion pairs must be present in solution or formed during the rotation process) or the spectra are counter-ion dependent (indicating the presence of contact ion pairs in solution) are represented by an open circle. Some authors seem to have assumed that rotations in this last category would always be faster than those for the free anions, basing their assumption on the idea, either that contact ion pairs or ' covalent organometallics ' will be isostructural with the isoelectronic hydrocarbon,[26] or that ion pairing removes electron density from the organic anion, and so weakens the C–C π-bonds. Although the second of these ideas is doubtless correct the first is highly questionable. It is known, for example, that benzyl-lithium has a structure, in the solid state, in which lithium bridges between carbon atoms[31] and a similar structure has been proposed for allyl-lithium.[3] In such systems rotations about C–C bonds must break the carbon–metal bond and this in turn must increase the barrier to rotation. As may be seen from Figure **3** some of the rotational barriers for the ion pairs are indeed higher than those expected for the free anion.

TABLE 4

Rates of phenyl rotation for *trans,trans*-diphenylpropenide ion in 15% [$^2H_3$]methyl t-butyl ether–85% liquid ammonia, T_2 taken as 0.063 6 s in all cases

Counter-ion	Temp. (°C)	k_{exch}/s^{-1}
Na^+	−37.8	430
Li^+	−42.7	253
Na^+	−42.7	245
K^+	−42.2	220
Na^+	−45.6	154
Li^+	−48.6	130
Na^+	−48.6	111
K^+	−48.6	119
Na^+	−57.6	65
Na^+	−61.2	40

EXPERIMENTAL

Preparation of ^{13}*C-Enriched Anion Precursors.—Benzoic* [^{13}C]*acid*. Commercially available enriched barium carbonate (90.7 atom % ^{13}C; Merck, Sharp, and Dohme) was diluted to 21.5 atom % with natural abundance barium carbonate and used to generate ^{13}C-enriched carbon dioxide. This was converted into benzoic acid by reaction with phenylmagnesium bromide, by using the method and apparatus described by Dauben *et al.*[32] Barium [^{13}C] carbonate (3.5 g, 18 mmol) gave benzoic [^{13}C]acid, m.p. 119—121 °C (1.78 g, 82%).

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[31] J. J. Brooks and G. D. Stucky, *J. Amer. Chem. Soc.*, 1970, **92**, 1150; J. J. Brooks, W. Rhine, and G. D. Stucky, *ibid.*, 1972, **94**, 7339.

[32] W. G. Dauben, J. C. Reid, and P. E. Yankwich in ' Organic Synthesis with Isotopes, Part I,' ed. A. Murray and D. Lloyd Williams, Interscience, New York, 1958, p. 87.

[1-^{13}C]*Acetophenone*. Benzoic [^{13}C]acid (2.18 g, 18 mmol) was dissolved in thionyl chloride (4 cm^3, 34 mmol) and refluxed for 2 h. The excess of reagent was evaporated off under reduced pressure and the last traces were removed by bulb distillation [100 °C (bath) and 20 mmHg]. Gilman and Nelson's method for the conversion of this acid chloride into propiophenone [33] was modified as follows. Methyl bromide, dried by passage over calcium chloride, was bubbled into a three-necked flask equipped with a gas inlet, a nitrogen inlet, a solid CO_2 condenser, and a magnetic stirrer, and containing ether (30 cm^3), magnesium (0.8 g, 34 mmol), and a crystal of iodine. The rate of addition was adjusted to produce gentle refluxing and continued until only a small quantity of magnesium remained. The whole of the Grignard solution was transferred by syringe into a second three-necked flask equipped with a mechanical steel paddle-stirrer. Gilman and Nelson's procedure [33] was then followed exactly for the addition of the cadmium chloride (3.14 g, 17 mmol), benzene (40 cm^3), and the [α-^{13}C]benzoyl chloride in benzene (7 cm^3). In the final stage of isolation the solution was concentrated with a rotary evaporator. Bulb distillation [100 °C (bath) and 20 mmHg] gave [1-^{13}C]-acetophenone (1.67 g, 77%), homogeneous by n.m.r., J_{CCH} 6.0 Hz.

3-(4-*Fluorophenyl*)-1-*phenyl*[1-^{13}C]*propene*. This was prepared in the same manner as the unlabelled material [1a] from [1-^{13}C]acetophenone (0.96 g, 8 mmol). The final chromatography gave two fractions: a mixed fraction of *cis*- and *trans*-olefins (300 mg; g.l.c. showed 14% *cis*-olefin, 83% *trans*-olefin, and 2% *trans*-positional isomer) followed by a *trans*-olefin fraction (340 mg; g.l.c. showed 95% *trans*-olefin, 2% *cis*-olefin, and 2% *trans*-positional isomer). The *cis*-olefin showed δ_H ($CDCl_3$) 3.62 (2 H, dd, J 7.5 and 1.5 Hz, CH_2) and 5.80 (1 H, dt, J 11.5 and 7.5 Hz, $=C\mathit{H}\cdot CH_2$), δ_C ($CDCl_3$) 130.3 ($PhCH=$). The ^{13}C satellites in the ^{1}H n.m.r. spectrum of the second fraction (*trans*-olefin) showed first-order splitting: δ_H ($CDCl_3$) 6.41 (ddt, J_{CH} 154, J_{HH} 16 and 1.5 Hz, $PhC\mathit{H}=$), δ_C ($CDCl_3$) 131.4 ($PhCH=$). The total yield of olefin was 640 mg (89% *trans*, 8% *cis*, and 2% *trans*-positional isomer) (38%) based on acetophenone.

[^{2}H$_3$]*Methyl t-Butyl Ether*.—The procedure of Norris and Rigby [34] for the preparation of ethyl t-butyl ether was modified as follows. Concentrated sulphuric acid (2 cm^3, 40 mmol) was added to ice-cooled [^{2}H$_4$]methanol (Fluorochem; 10 cm^3, 0.25 mmol). t-Butyl alcohol (23 cm^3, 0.25 mol) was added and the solution refluxed for 3 h. The mixture was rapidly distilled through a 6 in Vigreux column and the fraction of b.p. 51—56 °C collected. This was dried first with sodium wire and then by refluxing with lithium aluminium hydride, and finally refractionated, b.p. 54—55 °C. The ether (7 g, 32%) was stored over 3A molecular sieve under nitrogen. It showed δ_C ($CDCl_3$) 27.07 [$C(\mathit{C}H_3)_3$] and 72.70 [$\mathit{C}(CH_3)_3$]; at a signal-to-noise ratio of 250 : 1 for the signal at δ 27.07 no other signals were observed.

Visible Absorption Spectra.—The apparatus is shown diagrammatically in Figure 4. The detachable part, J, was washed with 2N-hydrochloric acid, water, and acetone and dried in an oven. The side-arms, L and M, which provided access for cleaning were sealed off. A measured length of freshly obtained sodium wire from a standard die (0.11 mmol) was placed in K together with one or two small crystals of ferric chloride. The apparatus was at once attached to the vacuum line (*via* G) and evacuated. Ammonia (*ca.* 3 cm^3), which had been dried with sodium and was stored in bulbs attached to the manifold of the vacuum line, was condensed into K, which was cooled with liquid nitrogen. The liquid nitrogen was replaced by a bath of solid CO_2–diethyl ketone (−42° C) and with tap B closed and the syringe needle E removed the apparatus was filled with oxygen freed nitrogen by opening tap C. A slow stream of nitrogen was passed through the apparatus until the sodamide had formed (usually *ca.* 2 h). A concentrated solution of the anion precursor [diarylpropene (0.10 mmol)] in dry diethyl ether was added from a syringe with a needle sufficiently long to extend into K. A cherry-red colour was instantly observed. The solution was frozen in liquid nitrogen, tap C closed, tap B opened, and the apparatus evacuated. After a single freeze–pump–thaw cycle the solvent was frozen and, after evacuation to 10^{-4} mmHg, the apparatus was detached by sealing off at the constriction N. After testing at room temperature to make sure that the cell could withstand the pressure of the ammonia, a small portion of the solution was filtered through the sinter H into the cell I and diluted by distillation of the rest of the solvent from K. The spectra were determined with a Unicam SP 800 or SP 8000 instrument. For variable temperature studies the cell I was cooled by immersion in ethanol (precooled to −70 °C) and contained in a Dewar flask with optical windows. This was allowed to warm up slowly to room temperature. Spectra were recorded when the temperature had reached −55, −20, and +15 °C. A correction has been applied to the spectra shown in Figure 1 to allow for thermal expansion. It was shown that, in the region studied, there was no loss of resolution in using a Pyrex rather than a quartz cell.

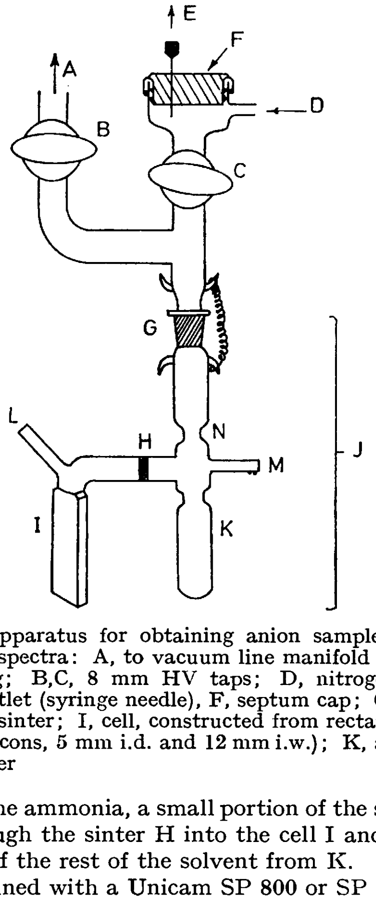

FIGURE 4 Apparatus for obtaining anion samples for visible absorption spectra: A, to vacuum line manifold evacuated to 10^{-4} mmHg; B,C, 8 mm HV taps; D, nitrogen inlet; E, nitrogen outlet (syringe needle), F, septum cap; G. B10 joint; H, grade 3 sinter; I, cell, constructed from rectangular Pyrex tubing (Jencons, 5 mm i.d. and 12 mm i.w.); K, anion generation chamber

N.m.r. Spectra.—A similar procedure was employed except that instead of adding the anion precursor by syringe it was placed in a side arm attached to K. The anion was then

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[33] H. Gilman and J. F. Nelson, in ref. 32, p. 663.

[34] J. F. Norris and G. W. Rigby, *J. Amer. Chem. Soc.*, 1932, **54**, 2088.

formed by pouring the sodamide–liquid ammonia into this side arm after the apparatus had been detached from the vacuum line. The ether was, however, added by syringe as before.

^1H N.m.r. spectra were recorded with a Brüker HX-90 instrument using the conventional frequency sweep mode of operation and the $C(CH_3)_3$ resonance of the methyl t-butyl ether as internal lock. To take into account local variations in scale linearity additional calibrations were made close to the signals of interest, especially those due to the benzylic protons. Chemical shifts were recorded relative to the lock and were converted to the δ (Me_4Si) scale by adding 1.11 p.p.m. If the solution was not filtered there was a substantial loss of resolution.

^{13}C N.m.r. spectra were determined with the same instrument at 22.62 MHz using Fourier transform and wide-band ^1H decoupling. The deuterium of $CD_3{\cdot}O{\cdot}C(CH_3)_3$ was used as internal lock. The minimum theoretical linewidth was *ca.* 1.5 Hz and chemical shifts were accurate to within ± 0.07 p.p.m. Chemical shifts were taken relative to the $OC(CH_3)_3$ signal of the lock and converted to a δ (Me_4Si) scale by adding 27.07 p.p.m. In the variable temperature studies, temperature measurement was achieved by using a calibrated thermometer in methanol in a ^{13}C n.m.r. tube and inserted into the probe under the same constant conditions of air-flow, spinning rate, *etc.* as were used in determining the spectrum. Measurements at the beginning and end of the run showed a maximum drift of 0.5 °C.

It was found that new n.m.r. tubes could normally withstand the pressure of liquid ammonia up to 25 °C but after they had been used two or three times they seemed to be weakened and almost inevitably exploded.

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