# Organic Anions. Part 5.[1] On the Nature of the Prop-2-ynyl/Allenyl Anion

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*Ab initio* MO calculations on the prop-2-ynyl/allenyl anion (1) suggest that it adopts an ' allene-like ' geometry (4) and it seems likely that this is associated with a concentration of charge at the less substituted (CH) end of the molecule. On the other hand both CNDO II MO calculations and spectroscopic studies on the 1,3-diphenyl substituted anion (9) suggest that it adopts a ' planar ' geometry (Figure 2) with the charge concentrated at the more substituted (CHPh) end of the molecule. This dependence of geometry and charge distribution on the degree of conjugation allows a number of earlier, apparently contradictory observations, to be rationalised.

PROP-2-YNYL/ALLENYL anions are known to be intermediates in the base-catalysed isomerisation of acetylenes [2,3] and the corresponding organometallic derivatives are important intermediates in the synthesis of both acetylenes and allenes. However, the geometries of these anions and the way in which charge is distributed within them remain obscure. The unsubstituted anion (1) may be formally derived by removal of a proton from either propyne or allene. If these operations are performed without rehybridisation the first produces the anion in an ' acetylene-like ' geometry (2) in which the $CH_2$ centre is $sp^3$ hybridised and the CH centre $sp$ hybridised whereas the second leads to an ' allene-like ' anion (4), in which both $CH_2$ and CH centres are $sp^2$ hybridised. It is known, however, that carbanionic centres next to conjugating substituents tend to rehybridise in order to maximise that conjugation [4] (compare, for example, the geometries of propene with the allyl anion [5] or toluene with the benzyl anion [6]) and

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[1] Part 4, R. J. Bushby and A. S. Patterson, *J. Organometallic Chem.*, 1977, **132**, 163.

[2] R. J. Bushby and G. H. Whitham, *J. Chem. Soc. (B)*, 1969, 67.

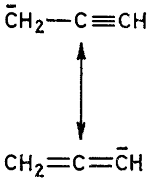
[3] R. J. Bushby and G. H. Whitham, *J. Chem. Soc. (B)*, 1970, 563; R. J. Bushby, *Quart. Rev.*, 1970, **24**, 585; G. Pourcelot and C. Georgoulis, *J. Chim. phys.*, 1974, **71**, 1393.

[4] D. J. Cram, ' Fundamentals of Carbanion Chemistry,' Academic Press, 1965, Chapters 2 and 3.

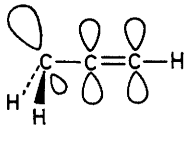
[5] D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, 1969, **14**, 370; P. Merlet, S. D. Peyerimhoff, R. J. Buenker, and S. Shih, *J. Amer. Chem. Soc.*, 1974, **96**, 959.

[6] S. P. Patterman, I. L. Karle, and G. D. Stucky, *J. Amer. Chem. Soc.*, 1970, **92**, 1150; J. J. Brooks, W. Rhine, and G. D. Stucky, *J. Amer. Chem. Soc.*, 1972, **94**, 7339.

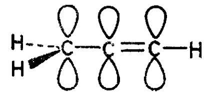
application of this principle to either (2) or (4) suggests an alternative ' planar ' geometry for the anion (3) which is intermediate between the two. In this the $CH_2$ centre is $sp^2$ hybridised and the CH centre *sp* hybridised. The ' acetylene-like ' geometry (2) is probably associated with concentration of charge at the $CH_2$ end of the molecule and the ' allene-like ' geometry (4) with concentration of charge at the CH end. For the ' planar ' geometry (3) simple HMO calculations suggest that the charge will be greatest at the $CH_2$ end [2] of the molecule.



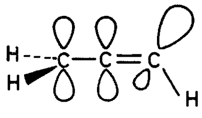
(1)



(2) 'Acetylene-like'



(3) 'Planar'



(4) 'Allene-like'

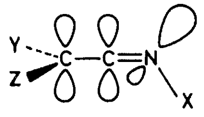
Cram has argued that this anion should prefer an ' allene-like ' geometry as this concentrates the excess charge in an orbital with a high degree of ' *s* ' character.[4] His case is strengthened by the observation that most of the isoelectronic ketene imines (5) adopt a geometry * which is a compromise between the planar and allene-like forms [7] and the $^{13}C$ n.m.r. studies of the lithium salt of anion (1) in tetrahydrofuran (THF) by van Dongen.[8] Particularly significant here is the low field position of the signal for the central carbon atom ($\delta_C$ 196.4) as this is in the region expected for the central carbon atom of an allene.[9] On the other hand, in this solvent, the lithium salt of anion (1) will certainly be contact ion paired and may well be more highly aggregated [10] and this could affect its geometry. An allene-like geometry is also suggested in the MO calculations of Gründler [11] but some of the other conclusions of this paper, for example the prediction of an unsymmetrical structure for the allyl anion, seem suspect.

By way of contrast our earlier studies of anions (6) and (7) [2] suggested a natural ' preference ' for the charge to be concentrated at the more highly substituted end of the molecule and hence we favoured the ' acetylene-like ' geometry or the ' planar ' geometry shown. Also the work of Köbrich on the cyclopropyl-substituted anion (8) seems to definitely indicate an ' acetylene-like ' geometry.[12]

It is also interesting to note that the prop-2-ynyl/allenyl radical adopts a planar structure with the free spin concentrated at the ' $CH_2$ ' end [13] and similarly the prop-2-ynyl/allenyl cation adopts a planar structure with the majority of the charge, once again, concentrated at the ' $CH_2$ ' end of the molecule.[14]

In an attempt to clarify the situation for the carbanions we have studied the spectroscopic properties of anion (9) and performed MO calculations both on this anion and the parent anion (1).

$^1H$ *N.M.R. Spectrum of the Anion* (9).—The 1,3-diphenyl substituted anion (9) can be generated in the same manner as the 1,3-diphenylallyl anions (10) studied previously; [15] that is, by treating the corresponding hydrocarbon (in this case diphenylpropyne) with sodamide or potassamide in liquid ammonia at —42 °C.[15,16] Unfortunately, however, the reaction of 1,3-diphenylpropyne was not as clean as the reaction of 1,3-diphenylpropene.[16] Even after optimisation of the reaction conditions, acidification of anion solutions gave only a 65—70% recovery of monomeric material (1,3-diphenylpropyne and 1,3-diphenylallene), the remaining



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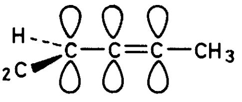

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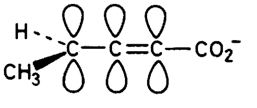

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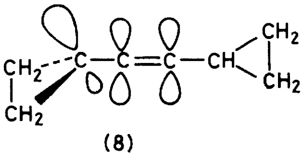

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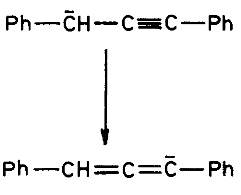

(9)

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* The presence of the nitrogen is, however, likely to bias the geometry towards the allenyl form [*cf.* aniline and the benzyl anion (D. G. Lister and J. K. Tyler, *Chem. Comm.*, 1966, 152)].

[7] R. R. Naqvi and P. J. Wheatley, *J. Chem. Soc.* (*A*), 1970, 2053 and references therein.

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

[9] J. B. Stothers, ' Carbon-13 N.M.R. Spectroscopy,' Academic Press, 1972.

[10] 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.

[11] W. Grundler, *Tetrahedron*, 1970, **26**, 2291.

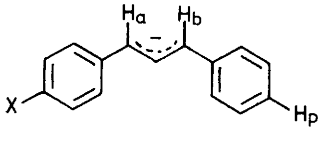
[12] G. Köbrich, D. Merkel, and K. Imkampe, *Chem. Ber.*, 1973, **106**, 2017.

[13] F. Bernardi, C. M. Camaggi, and M. Tiecco, *J.C.S. Perkin II*, 1974, 518; W. Ahrens, K. Wieser, and A. Berndt, *Tetrahedron Letters*, 1975, 1313.

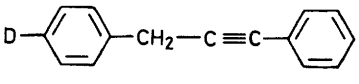
[14] C. U. Pittman, G. Wilemon, J. E. Fojtasek, and L. D. Kispert, *J. Phys. Chem.*, 1975, **79**, 2443; L. Radom, P. C. Hariharan, J. A. Pople, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1976, **98**, 10.

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

[16] R. J. Bushby and G. J. Ferber, *J.C.S. Perkin II*, 1976, 1683.

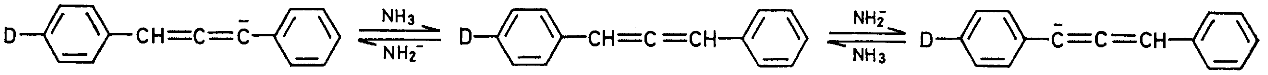


(10)



(11)

30—35% being a complex mixture containing some dimers (see Experimental section). Whilst it is possible that some of these by-products were formed on work-up[17] it seems that some were actually formed during anion generation.[18] These show up in the $^1$H n.m.r. spectrum (Figure 1) as a broad envelope of peaks δ 7—7.5. The other signals, however, appear to be associated with the anion itself. The peak at δ 3.44 is assigned to the benzylic hydrogen and the pattern for the aromatic region δ 6—7 is very similar to that for other, related anions with the signals for the *para* hydrogens (δ 6.53 and 6.03) coming at higher field than those for the *ortho*- and *meta*-hydrogens. As expected,[19] the spectrum is virtually independent of counter-ion (sodium or potassium) indicating that solvent-separated rather than contact ion pairs are the predominant species in solution.[20] It is interesting to note that the signal for the benzylic hydrogen of the anion (9) is at higher field (δ 3.44) than that for the anion (10) (δ 4.71; X = H), indicating that the charge on this carbon atom is probably higher. This does not, however, enable the relative charges of the two ends of the allenyl–prop-2-ynyl unit to be determined as the other benzylic position does not carry a hydrogen atom. Fortunately, previous work[19] on the diarylallyl anions (10; X ≠ H) has shown that there is a good linear relationship between the chemical shifts of $H_b$ and $H_p$ and, hence, that the chemical shifts of *para*-hydrogens may be used as a secondary indication of the charge at a benzylic position when no benzylic hydrogen is present.[21] Assignment of the two *para* hydrogen signals in the spectrum of the anion (9) should, therefore, give some indication of the relative charges of the benzylic positions. In an attempt to assign these signals the deuteriated diphenylpropyne (11) was synthesised and treated with sodamide–liquid ammonia. It was found, however, that the signals for *both para*-hydrogens were equally diminished. This is probably the result of equilibration through a small concentration of the allene:



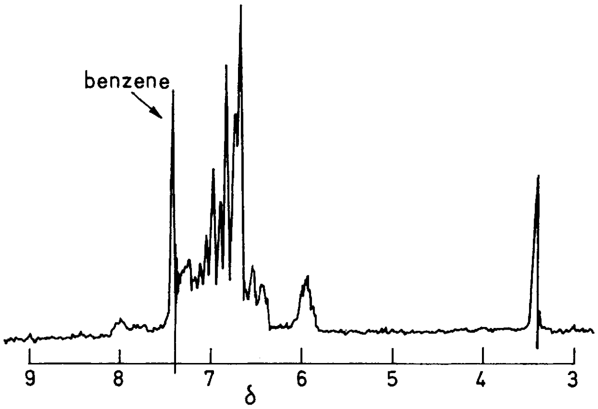


FIGURE 1 $^1$H N.m.r. spectrum of the anion (9) (*ca.* 0.4M) in liquid ammonia with benzene as internal standard

Fortunately this anion can also be generated by using butyl-lithium in hexane–THF, and in this medium, not only is anion formation irreversible, but, relative to ammonia, the *para* hydrogen signals (δ 6.42 and 6.07) are more cleanly resolved from the other aromatic hydrogen resonances. When the deuteriated anion precursor (11) was employed only the signal at δ 6.42 was observed. This indicates that the charge at the ' CHPh ' end of the molecular is greater than that at the ' CPh ' end.

$^{13}$C *N.M.R. Spectrum of the Anion* (9).—The $^{13}$C n.m.r. spectrum of the anion (9) in liquid ammonia, like the proton spectrum, shows a rather complex series of peaks in the ' aromatic ' region (δ 110—150), some of which are, undoubtedly, due to by-products of the anion generation, and assignments in this area are difficult. The following features of the spectrum are, however, significant.

First the high field value for the *C*HPh benzylic carbon resonance ($\delta_c$ 54.2, assigned by $^{13}$C enrichment and selective decoupling with the proton signal at $\delta_H$ 3.44). This is at higher field than the corresponding signal for the CHPh benzylic carbon in the anion (10) ($\delta_c$ 90.3, X = H) and is indicative of a high negative charge at this position. Secondly the $^{13}$C/$^1$H one-bond coupling constant of 157 Hz for this signal indicates $sp^2$ hybridisation.[19] Thirdly, in contrast to the results of van Dongen on the parent anion (1), no signal could be detected below δ 150. This eliminates the possibility of an ' allene-like ' geometry and together with the coupling constant for the benzylic hydrogen indicates that the anion adopts a ' planar ' geometry. The signal for the other benzylic carbon is rather difficult to assign but is probably that at δ 99.5. This is unaffected by proton

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[17] E. V. Dehmlow, *Chem. Ber.*, 1967, **100**, 3260; *Angew. Chem. Internat. Edn.*, 1972, **11**, 322.

[18] R. Eidenschink and T. Kauffmann, *Angew. Chem. Internat. Edn.*, 1972, **11**, 292.

[19] R. J. Bushby and G. J. Ferber, *J.C.S. Perkin II*, 1976, 1688.

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

[21] 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**, 514.

decoupling and, like the signal at δ 54.2, is enhanced in the $^{13}$C enriched material.

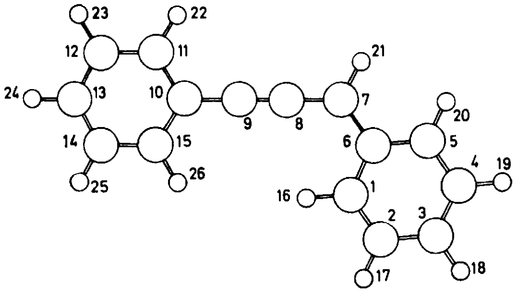

FIGURE 2 CNDO II results for anion (9)

Bond lengths (Å)

Aryl C–C = 1.39
C(6)–C(7) = 1.42
C(7)–C(7) = 1.38
C(8)–C(9) = 1.24
C(9)–C(10) = 1.40
Aryl C–H = 1.12
Benzyl C–H = 1.12

Angles (degrees)

C(6)–C(7)–C(8) = 125

Charges (electrons)

C(1) = −0.08
C(2) = +0.03
C(3) = −0.08
C(4) = +0.03
C(5) = −0.08
C(6) = +0.11
C(7) = −0.25
C(8) = +0.03
C(9) = −0.24
C(10) = +0.12
C(11) = −0.06
C(12) = +0.02
C(13) = −0.06
C(14) = +0.02
C(15) = −0.06

H(16) = −0.03
H(17) = −0.05
H(18) = −0.05
H(19) = −0.05
H(20) = −0.04
H(21) = −0.06
H(22) = −0.03
H(23) = −0.04
H(24) = −0.04
H(25) = −0.04
H(26) = −0.02

*CNDO II Calculations on Anions* (9) *and* (10) (X = H).—CNDO II calculations on the anions (9) and (10) (X = H) involving partial geometry optimisation (see Experimental section) and standard Pople–Segal parameters [22] resulted in the geometries and charge distributions shown in Figures 2 and 3. These geometries were also shown to be stable with respect to rotation of either or both of the phenyl groups or rehybridisation of the benzylic carbon atoms. It should be noted that, in agreement with the spectroscopic results, the negative charge at C(7) of (9) is greater than that at C(9) of (9) or at C(7) of (10) although neither of the calculated differences is as large as might be expected from the magnitudes of the differences in chemical shift. The 'opening out' of the angles from the expected 120° is similar to that calculated for the pentadienyl system and presumably has a similar explanation.[1]

*Electronic Absorption Spectrum of the Anion* (9).—The electronic absorption spectrum of anion (9) in liquid ammonia shows a single smooth peak ($\lambda_{max.}$ 492 nm) which is virtually unaffected by counter ion ($Li^+$, $Na^+$, and $K^+$) or temperature (−55 to +18 °C). Its position, relative to the anion (10) [19] under the same conditions ($\lambda_{max.}$ 550 nm, shoulder 525 nm), is rather hard to explain as application of Krauch's rule [23] suggests a value for anion (9) of 550 + 34 = 584 nm. If the geometries predicted by the CNDO II calculations and confirmed by the n.m.r. data are correct then the deviation from the expected $\lambda_{max.}$ value cannot be attributed to conformational causes as the geometrical relationship between (9) and (10) is the same as that between any cumulated and conjugated polyene. A more likely explanation lies in the fact that the anions (9) and (10) are odd alternant systems whereas the rule was derived by consideration only of even alternant systems.

*The Reaction of the Anion* (9) *with Acids*.—Treatment of a liquid ammonia solution of the anion (9) with ammonium chloride at room temperature gave a 3.8 : 1.0 mixture of 1,3-diphenylpropa-1,2-diene and 1,3-diphenylpropyne and, similarly, acidification of a THF–hexane solution with 2N-hydrochloric acid at room temperature gave a 3 : 1 mixture of allene : acetylene. This case, in which there is predominant protonation at the less highly charged benzylic position, does not necessarily conflict with the results obtained earlier for the diphenylallyl systems [24] since, for the anion (9), the steric/solvation environments of the two benzylic positions differ. The possibility also remains that in all these systems the position of protonation is determined by a combination of 'charge' and 'product stability' factors [*,24] and, in this particular instance, there is a very large stability factor in favour of formation of the allene. It

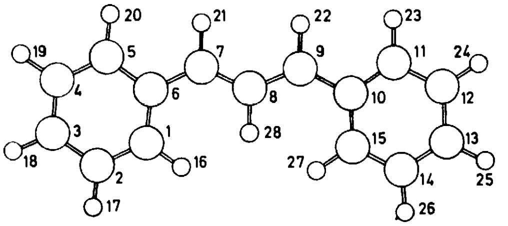

FIGURE 3 CNDO II results for the anion (10)

Bond lengths (Å)

Aryl C–C = 1.39
C(6)–C(7) = 1.43
C(7)–C(8) = 1.38
Aryl C–H = 1.12
Other C–H = 1.12

Angles (degrees)

C(6)–C(7)–C(8) = 130
C(7)–C(8)–C(9) = 131

Charges (electrons)

C(1) = −0.07
C(2) = +0.03
C(3) = −0.07
C(4) = +0.02
C(5) = −0.07
C(6) = +0.10
C(7) = −0.22
C(8) = +0.11

H(16) = −0.02
H(17) = −0.05
H(18) = −0.05
H(19) = −0.05
H(20) = −0.03
H(21) = −0.06
H(28) = −0.06

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[*] The rationale behind using a combination of product stability and charge control factors to determine the position of attack in ambident systems (T. N. Huckerby, N. A. J. Rogers, and A. Sattar, *Tetrahedron Letters*, 1967, 1113) is more readily appreciated by considering intersecting energy profiles (as M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 1938, **34**, 11; K.-L. Mok and M. J. Nye, *J.C.S. Perkin I*, 1975, 1810) than by the approach used previously (ref. 24).

[22] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, 1970.

[23] H. Krauch, *J. Chem. Phys.*, 1958, **28**, 898.

[24] R. J. Bushby and G. J. Ferber, *J.C.S. Perkin II*, **1976**, 1695.

was not possible to determine the exact position of equilibrium between the two isomers since the allene was not stable to g.l.c. conditions but prolonged treatment with base followed by preparative t.l.c. suggested that the allene is favoured by a factor of at least 19 to 1.

Ab initio *MO Calculation on the Anion* (1).—A population analysis on the results of CNDO II calculations on the anion (1) confirmed the expected pattern of charge distribution. The geometry (4) was associated with a concentration of charge at the CH end of the molecule and geometries (2) and (3) with a concentration of charge at the $CH_2$ end of the molecule. The predicted geometry of the system was, however, found to be dependen ton the parameterisation employed. It was, therefore, decided to perform a series of *ab initio* Hartree–Fock MO calculations. The basis set used was Dunning's 4*s* 3*p* contraction of Huzinaga's 9*s* 5*p* set of Gaussian primitives for carbon [25] and a previously reported set for hydrogen.[26] Diffuse functions were not added to this basis set since no undue 'peaking' of atomic orbital expansion coefficients was found for the occupied orbitals. The anion was initially assumed to be planar with the C–C–C–H portion linear. Optimisation of the bond lengths and angles while maintaining a linear –C–C–H fragment resulted in the geometry shown in Figure 4. This was shown to be stable with respect to rehybridisation of the $CH_2$ centre but not to bending of the terminal CH hydrogen out of the plane. A second series of calculations, in which the C–C–H angle was also varied, produced the minimum energy allene-like geometry shown in Figure 5

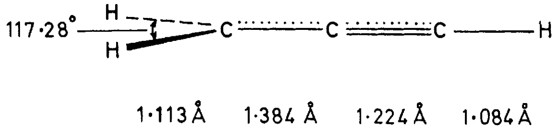

FIGURE 4 *Ab initio* MO calculation. Optimised geometry for the 'planar' anion (1)

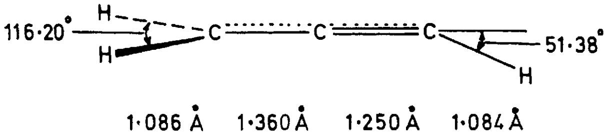

FIGURE 5 *Ab initio* MO calculation. Optimised geometry for the 'allene-like' anion (1)

Table 1 summarises energies and virial ratios obtained from which it may be seen that the *sp* basis set predicted an energy difference between the planar and allene-like forms of 0.004 765 a.u. (3.0 kcal $mol^{-1}$) in favour of the allene-like structure. Since it is known that calculated inversion barriers are very sensitive to the inclusion of polarisation function [27] the calculations were repeated for the geometries shown in Figures 4 and 5 with polarisation functions included in the basis set. A full complement of *d*-type functions, each constructed as a two term Gaussian expansion of a Slater 3*d* function of $\zeta = 2.40$, was used for the carbon atoms, and *p* functions of Gaussian exponent 1.0 were added to the hydrogen sets. As may be seen from the Table this increased the energy difference substantially (to 0.011 345 a.u.; 7.1 kcal $mol^{-1}$) but still showed that the allene-like form is predicted to be the more stable.

TABLE 1

*Ab initio* results for calculations on the anion (1)

| Geometry | Basis set | Energy (a.u.) | $V/T$ |
|---|---|---|---|
| Figure 4 | Without polarisation functions | −115.191 672 | 2.000 36 |
| Figure 5 | Without polarisation functions | −115.196 437 | 1.998 94 |
| Figure 4 | With polarisation functions | −115.239 798 | 2.001 18 |
| Figure 5 | With polarisation functions | −115.251 143 | 1.999 88 |

*Conclusions*.—The prediction that the parent prop-2-ynyl/allenyl anion (1) prefers an allene-like geometry is consistent with the spectroscopic results of van Dongen [8] and the 'flattening' of the system with increasing conjugation has a number of parallels in other carbanionic systems.[4] What is interesting about this particular anion is that this flattening out is apparently associated with a transfer of charge from one end of the molecule to the other. If it is assumed that $CO_2^-$, like the phenyl group, is a sufficiently strongly conjugating substituent to cause flattening of the anion then the relative stabilities of anions (6) and (7) may also be understood in terms of the effect of substituents on the preferred charge distribution in the planar form.[2] The preference of the anion (8) for an acetylene-like form is probably a direct consequence of ring strain.[12] The finding that the lithium derivatives of both anions (1) [28] and (9) [29] in hydrocarbon medium show a strong allene stretching absorption in their i.r. spectra is probably a result of aggregation and/or contact ion pairing.[29] The effects of ion pairing on anion geometry are presently under investigation.

## EXPERIMENTAL

1,3-*Diphenylpropyne*.—This compound was prepared by the reaction of benzyl tosylate [30] with the Grignard derivative of phenylacetylene by the method of Johnson *et al.*;[31] yield 63%, b.p. 89 °C at 0.03 mmHg (lit., 72%, 150—160 °C at 4 mmHg), $\delta_H$ ($CCl_4$) 7.1—7.4 (10 H, m, ArH) and 3.77 (2 H, s, $CH_2$); $\delta_C$ ($CDCl_3$) 25.7 ($CH_2$), 82.8 (C≡*C*–$CH_2$), 87.7 (Ph–*C*≡C), 123.9 (1-ArC), 126.8 (4′-ArC), 127.9 (4-ArC), 128.1, 128.3, 128.6 (3, 5, 2′, 6′, 3′, and 5′-ArC), 131.8 (2,6-ArC), and 136.9 (1′-ArC).

An alternative preparation,[32] using benzyl bromide instead of the tosylate, was found to be less satisfactory

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since the product contained *ca.* 29% of dibenzyl which could only be removed by fractionation through a spinning band column.

1,3-[p-$^2$H]*Diphenylpropyne* (XI).—*p*-Bromotoluene was converted into [*p*-$^2$H]toluene and thence into [*p*-$^2$H]benzyl chloride and [*p*-$^2$H]benzyl alcohol.[33] The [*p*-$^2$H]benzyl alcohol was converted into the tosylate and thence the acetylene as before. Mass spectroscopy showed that *ca. 80% of the material* contained deuterium labelling.

1,3-*Diphenyl*[3-$^{13}$C]*propyne*.—Benzoic acid (1.78 g, 15 mmol, 26.7% atom $^{13}$C in the $CO_2H$ group)[19] in dry ether (22.5 ml) was added dropwise during 10 min to a stirred solution of lithium aluminium hydride (0.7 g, 18 mmol) in dry ether (27 ml) under an atmosphere of nitrogen. After 1 h the solution was surrounded with ice and the excess of hydride was destroyed with water. The reaction mixture was acidified (1M-sulphuric acid) and extracted with ether. The combined ether extracts were washed with aqueous sodium hydroxide and water, dried, and concentrated on a rotary evaporator. Bulb distillation of the residue (70 °C at 25 mmHg) yielded [α-$^{13}$C]benzyl alcohol, 1.20 g, 76%. The $^1$H n.m.r. spectrum showed *J*(C/H) 142.7 Hz.

This was converted into the tosylate and thence the acetylene as before. The $^1$H n.m.r. spectrum of the acetylene showed *J*(C/H) 131.0 Hz.

1,3-*Diphenylpropa*-1,2-*diene*.—A solution of 1,3-diphenylpropyne (500 mg) in 0.1N-methanolic sodium methoxide was set aside at room temperature for 49 h. The crude product was subjected to preparative t.l.c. on silica gel, four elutions with light petroleum being used to yield the following fractions.

(1) (Apparent $R_F$ 0.7), 1,3-diphenylpropa-1,2-diene (166 mg, 33%), m.p. after low temperature recrystallisation from light petroleum 43.5—45 °C (lit.,[32] 50 °C), $\nu_{max.}$ ($CHCl_3$) 1 938 (C=C=C) cm$^{-1}$; $\delta_H$ ($CCl_4$) 7.37 (10 H, s, ArH), and 6.48 (2 H, s, C*H*=C=C*H*); $\delta_C$ ($CDCl_3$) 98.5 (Ph*C*H=), 127.0, 127.4, 128.8 (2, 3, 4, 5, 6-ArC), 133.6 (1-ArC), and 207.9 (CH=*C*=CH).

(2) (Apparent $R_F$ 0.6), 1,3-diphenylpropyne (189 mg, 37%).

(3) (Apparent $R_F$ 0.1—0.2). A complex mixture of other products.

*Spectroscopic Studies*.—The methods for anion generation and spectroscopic studies in liquid ammonia were the same as those described previously[16,19] as were the concentrations employed. The method for generation using butyllithium–hexane–THF was based on that of Bates *et al.*[34]

*Reaction of Anion Solutions with Acid*.—The reaction of an ammonia solution with ammonium chloride was carried out in duplicate in the same manner as that described previously.[24] The reaction of a THF–hexane solution with dilute aqueous acid was arrived at simply by adding the acid rapidly from a syringe. The composition of the product produced in each case was determined by integration of the $^1$H n.m.r. signals at δ 6.48 and 3.77 immediately after quenching. The product ratios were checked (roughly) by preparative t.l.c. Repeated chromatography of the complex mixture of by-products (lower $R_F$ than either monomer) gave two compounds in an apparently homogeneous state (t.l.c. with several solvents). Both showed parent ions *m/e* 384 (corresponding to dimers) in the mass spectrum.[17,18]

*CNDO II MO Calculations on the Anions* (9) *and* (10).—These calculations were carried out as described previously[1] except that, for these larger molecules, it was found that re-using coefficients generated for one geometry for the initial ' guess ' in calculations on a related geometry resulted in a substantial saving in computer time.

For anion (10) (X = H, Figure 3) it was initially assumed that the molecule was planar with a further plane of symmetry bisecting the angle C(7)–C(8)–C(9). It was further assumed that all aromatic C–C bonds were of equal length, all aromatic C–H bonds were of equal length, and the bonds C(7)–H(21), C(8)–H(28), and C(9)–H(22) were of equal length. The bonds C(6)–C(7), C(7)–H(21), and C(8)–C(28) were assumed to bisect the angles C(1)–C(6)–C(5), C(6)–C(7)–C(8), and C(7)–C(8)–C(9) respectively. The remaining variables were then optimised as before,[1] angles to the nearest 1° and bond lengths to the nearest 0.01 Å. The resultant geometry (Figure 3) was shown to be stable with respect to rotation of the phenyl rings or rehybridisation of the benzylic carbon atoms.

For anion (9) (Figure 2) equivalent assumptions were made except that the bond lengths in the two aromatic rings were varied separately. Once again the resultant geometry was shown to be stable with respect to rotation of the phenyl rings or rehybridisation of the benzylic carbon atoms.

Ab initio *M.O. Calculations on Anion* (I).—These were performed using the MANYATOM SCF system on the UMRCC CDC 7600 computer.[35]

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