Structure and Conformation of Polynitrodiphenylmethanes and Related Carbanions

Marie-Paule Simonnin, Hai-Qi Xie, François Terrier,* and Jacques Lelievre
Laboratoire de Physicochimie des Solutions, URA-D0962 du CNRS, E.N.S.C.P. 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05
Patrick G. Farrell
Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal H3A 2K6, Canada

^1H and ^{13}C n.m.r. data are reported for a series of *ortho* and *para* nitro-substituted diphenylmethanes and related diphenylmethyl anions. In the case of the neutral molecules, a predominance of the skew conformation is suggested for mono- and di-*o* nitro-substituted derivatives, *e.g.* 2,4,4′-trinitro- and 2,2′4,4′-tetranitro-diphenylmethanes, while a perpendicular conformation is preferred by the tri-ortho nitro-substituted derivative, *e.g.* 2,2′,4,4′,6-pentanitrodiphenylmethane. ^{13}C shifts and $^1J_{C_\alpha H_\alpha}$ coupling constants indicate that, in all carbanions studied, the exocyclic α-carbon is sp^2 hybridized and carries only a small fraction of the negative charge. For carbanions with different substituents on the aromatic rings, *e.g.* 2,4,4′-trinitro- and 2,2′,4,4′,6-pentanitrodiphenylmethyl carbanions, the negative charge appears to be preferentially delocalized in the more substituted aromatic ring.

From arguments based upon the observed n.m.r. and u.v. spectroscopic data, the two rings in diphenylmethyl anions with up to two ortho nitro substituents are essentially coplanar, whereas steric interactions prevent such coplanarity in those with three or four such substituents.

The ionization of diphenylmethanes gives carbanions whose stabilities are largely governed by the extent of delocalization of their negative charge.[1–6] Although coplanarity of the two phenyl rings will represent the most effective geometry for this purpose,[7,8] it has been pointed out that such a favourable situation is probably difficult to achieve, even in the unsubstituted diphenylmethyl anion.[9] Thus, a geometry with somewhat twisted phenyl rings has been proposed for this carbanion to account for the necessity of avoiding close approach of the inner *ortho* hydrogen atoms.[9] No evidence for a twist angle could be obtained from the ^1H n.m.r. studies carried out on this species.[7]

Recent theoretical calculations have led to a reconsideration of ring twisting, indicating that the steric crowding of the inner *ortho* hydrogens may be eliminated in a coplanar diphenylmethyl anion providing that the α-carbon bond angle is enlarged from 120 to 139°.[9] No definitive proof for such a geometry could be obtained but support for a planar conformation has been obtained from a low temperature n.m.r. study of 4,4′-dideuteriodiphenyl methyl anion.[10]

In connection with the enhanced interest in the relationship between the intrinsic reactivities of carbon acids and the extent of the molecular, electronic, and solvational rearrangements which accompany the formation of carbanions with highly delocalized negative charges,[11–18] we have undertaken a thorough kinetic and thermodynamic study of the ionization of a series of nitro-diphenylmethanes. This series was constituted by accumulating NO_2 groups at the *para* and *ortho* positions of the two phenyl rings of diphenylmethane. For a better understanding of our kinetic results, ^1H, ^{13}C n.m.r., and u.v.–visible spectroscopy were used in a concomitant structural study. It is the results of this structural investigation that we report in this paper while the kinetic and thermodynamic results will be the subject of a forthcoming paper.

Results and Discussion

Tables 1–3 show the comparison between the proton and carbon n.m.r. data reported for the unsubstituted diphenylmethane (**1**) and its carbanion (**1**)$^-$ [7,8,19–21] with those for the nitro-substituted analogues studied in this work. These species are denoted with reference to the number of nitro substituents, *i.e.* 4,4′-dinitro [(**2**), (**2**)$^-$], 2,4,4′-trinitro [(**3**), (**3**)$^-$], 2,2′,4,4′-tetranitro [(**4**), (**4**)$^-$], 2,2′4,4′,6-pentanitro [(**5**), (**5**)$^-$], and 2,2′,4,4′,6,6′-hexanitro [(**6**), (**6**)$^-$] diphenylmethanes. Proton chemical shifts obtained for the two latter systems agree quite well with a previous report.[22]

Assignment of the various protons was straightforward in all cases. The ^{13}C spectra were assigned by using proton-coupled spectra, off-resonance and selective irradiation experiments. For the various nitrodiphenylmethanes, the ^{13}C chemical shifts were found to comply with the additivity of substituent effects of NO_2 groups. ^{13}C N.m.r. shifts for the symmetrical molecules (**2**), (**4**), and (**6**) were calculated from values reported by Buchanan *et al.* for (**1**)[20] and the NO_2 increments published by Levy *et al.*[23] and Breitmaier.[24,25] Differences between calculated and experimental values are all within 0.1 to 3 ppm, except for C(1) in (**6**) (*ca.* 7 ppm) (*cf.* the Experimental Section). This deviation is probably associated with the significant steric effects due to the presence of four *ortho* NO_2 groups in (**6**). An explanation in terms of twisting of these groups out of the plane of the aromatic ring, to minimize the steric hindrance may be excluded since it should also induce notable discrepancies between the calculated and experimental δ values for C(3) and C(5) while the observed differences are < 1 ppm. The observed ^{13}C substituent chemical shifts (SCS) additivity is consistent, as expected, with a negligible ring–ring interaction through the bridging methylene group. A quite different situation prevails in the carbanions and ^{13}C SCS could not be used to assign the quaternary carbons. These were assigned on the basis of long range J_{CH} values observed in proton-coupled spectra, but some ambiguities still remain and the tentative values are indicated in parentheses in Table 2.

Structures of Diphenylmethanes.—Diphenylmethane (**1**) does not have coplanar benzene rings in the solid state, as these are rotated by *ca.* 52° out of the plane containing the two C_{Ar}–C_α

Table 1. ^{1}H N.m.r. data for diphenylmethanes (**1**)–(**6**) and related carbanions (**1**)$^-$–(**6**)$^-$.^{a}

Compound	δH_α	δH(2)	δH(3)	δH(5)	δH(6)	δH(2′)	δH(3′)	δH(5′)	δH(6′)	J_{HH}
(**1**)^b	3.92									
(**1**)$^{-c}$	4.17	6.40$_6$	6.54$_5$							$^3J_{23}$ 8.32, $^4J_{24}$ 1.12, $^3J_{34}$ 6.89, $^4J_{35}$ 1.81
Δδ	+0.25									
(**2**)	4.26	7.55	8.17							$^3J_{23}$ + $^5J_{25}$ 8.4
(**2**)$^-$	5.64	6.96	7.67							$^3J_{23}$ + $^5J_{25}$ 9.3
Δδ	+1.38	−0.59	−0.50							
(**3**)	4.54		8.78	8.53	7.81	7.45	8.18			$^4J_{35}$ 2.4$_5$, $^3J_{56}$ 8.5$_5$, $^3J_{2'3'}$ + $^5J_{2'5'}$ 8.8$_6$
(**3**)$^-$	7.26		8.71	7.18	7.26	7.41	8.01			$^4J_{35}$ 2.4, $^3J_{56}$ 10.0$_5$, $^5J_{5\alpha}$ 1.0$_8$, $^3J_{2'3'}$ + $^5J_{2'5'}$ 8.9$_5$
Δδ	+2.72		−0.07	−1.35	−0.55	−0.04	−0.17			
(**4**)	4.80		8.82	8.50	7.61					$^4J_{35}$ 2.4, $^3J_{56}$ 8.5
(**4**)$^-$	7.50		8.65	7.70	7.56					$^4J_{35}$ 2.4, $^3J_{56}$ 9.4, $^5J_{5\alpha}$ 0.7
Δδ	+2.70		−0.17	−0.80	−0.05					
(**5**)	4.78		9.19				8.84	8.38	7.32	$^4J_{3'5'}$ 2.4, $^3J_{5'6'}$ 8.7
(**5**)$^-$	7.33		8.43				8.73	8.16	7.27	$^4J_{3'5'}$ 2.5, $^3J_{5'6'}$ 8.9, $^5J_{5'\alpha}$ 0.6
Δδ	+2.55		−0.76				−0.11	−0.22	−0.05	
(**6**)	5.08		9.07							
(**6**)$^-$	6.86		8.70							
Δδ	+1.78		−0.37							

^{a} δ in ppm relative to internal $SiMe_4$. *J* in Hz. Solvent [$^2H_6$]Me_2SO. ^{b} Data taken from ref. 19. ^{c} Data taken from ref. 19, $\delta_{H(4)}$ 5.64.

Table 2. ^{13}C Chemical shifts for diphenylmethanes (**1**)–(**6**) and related carbanions (**1**)$^-$–(**6**)$^-$.^{a}

Compound	δC_α	δC(1)	δC(2)	δC(3)	δC(4)	δC(5)	δC(6)	δC(1′)	δC(2′)	δC(3′)	δC(4′)	δC(5′)	δC(6′)
(**1**)^b	41.2$_5$	140.8	128.7	128.3	125.7								
(**1**)$^{-c}$	80.3	145.2	116.1	127.5	105.7								
Δδ	+39.0	+4.4	−12.6	−0.8	−20.0								
(**2**)	40.0	147.8	130.0	123.6	146.2								
(**2**)$^-$	106.5	145.7	124.5	121.4	133.7								
Δδ	+66.5	−2.1	−5.5	−2.2	−12.5								
(**3**)	37.2	140.6	148.6	120.2	146.4	127.6	134.4	145.9	129.9	123.6	146.2		
(**3**)$^-$	107.1	(133.4)	(130.0)	127.5	132.1	121.9	122.7	(147.8)	126.8	123.9	141.8		
Δδ	+69.9	(−7.2)	(−18.6)	+7.3	−14.3	−5.7	−11.7	(+1.9)	−3.1	+0.3	−4.4		
(**4**)	35.0	139.6	148.6	120.3	146.6	127.7	133.7						
(**4**)$^-$	100.9	(138.6)	(139.4)	124.1	(135.9)	124.4	126.0						
Δδ	+65.9	(−1.0)	(−9.2)	+3.8	(−10.7)	−3.3	−7.7						
(**5**)	31.5	131.6	151.1	124.0	147.1			138.6	147.8	120.0	146.3	127.1	131.7
(**5**)$^-$	102.2	(126.0)	141.7	126.7	(125.9)			(143.2)	(144.7)	120.9	(138.3)	126.3	127.1
Δδ	+70.7	(−5.6)	−9.4	+2.7	(−21.2)			(+4.6)	(−3.1)	+0.9	(−8.0)	−0.8	−4.6
(**6**)	27.6	129.4	150.4	123.6	146.8								
(**6**)$^-$	93.5	131.6	143.3	123.9	134.8								
Δδ	+65.9	+2.2	−7.1	+0.3	−12.0								

^{a} δ Relative to internal $SiMe_4$. Solvent [$^2H_6$]Me_2SO. ^{b} Data taken from refs. 19 and 20. ^{c} Data taken from ref. 20.

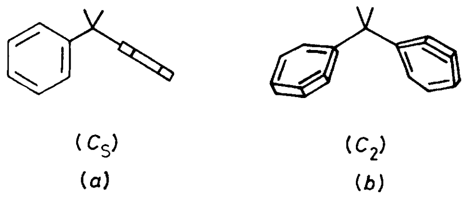

(C_S) (*a*) (C_2) (*b*)

Figure 1.

bonds.[26,27] However, it is generally agreed that (**1**) does not exhibit a fixed conformation in solution at room temperature. Figure 1(*a*) and (*b*), shows the most favoured forms.[28] In form (*a*), one ring is in the C_{Ar}–C–C_{Ar} plane and the other is perpendicular to it; form (*b*) represents the intermediate skew conformation.

In the present case, ^{1}H and ^{13}C n.m.r. spectra recorded at probe temperature indicate the equivalence of the two aromatic rings in 4,4′-dinitro- (**2**), 2,2′,4,4′-tetranitro- (**4**), and 2,2′,4,4′,6,6′-hexanitro- (**6**) diphenylmethanes. Furthermore, isochrony of proton and carbon nuclei in *ortho* and *meta* positions is observed in the symmetrically substituted aromatic ring(s) of (**2**), (**3**), (**5**), and (**6**). These results imply that rotation of these rings around the C_{Ar}–C_α bond is rapid on the n.m.r. time scale, even in the penta- and hexa-nitro derivatives.

It is interesting to look at the effects on the proton and carbon chemical shifts of one phenyl ring resulting from the introduction of an ortho NO_2 group into the other ring. For example, a comparison of 2,4,4′-trinitrodiphenylmethane (**3**) with 2,2′,4,4′-tetranitrodiphenylmethane (**4**) reveals no appreciable effect on H(3) and H(5) shifts but does show an upfield shift of H(6) (−0.20 ppm) in the latter compound. Similarly, nitration of (**4**) to give the 2,2′,4,4′,6-pentanitro derivative (**5**) results in a further high field shift of H(6′) (−0.29 ppm); concomitantly, there is an appreciable move of C(6′) to high field (−2.0 ppm). These effects are similar to, but smaller than, those reported by Montaudo *et al.*[28] as well as Buchanan *et al.*[20] for *ortho* methyl substitution of diphenylmethanes. These workers concluded that the preferred conformation in the tri-*o*-methyl diphenylmethanes is the perpendicular form (*a*) in which the one *ortho* proton is inside the π-cloud of the adjacent phenyl ring. Accordingly, the upfield *ortho* proton shift would arise from the shielding influence of the ring current in the remote phenyl

Table 3. $^{n}J_{^{13}\mathrm{CH}}$ Coupling constants for diphenylmethanes **(1)**–**(6)** and related carbanions **(1)**$^-$–**(6)**$^-$.^{a}

Compd.	$^1J_{C_\alpha H_\alpha}$	$^3J_{C_\alpha H_{2/6/2'/6'}}$	$^3J_{C_1H_{3/5}}$	$^2J_{C_1H_\alpha}$	$^1J_{C_3H_3}$	$^3J_{C_3H_5}$	$^2J_{C_4H_{3/5}}$	$^1J_{C_5H_5}$	$^3J_{C_5H_3}$	$^1J_{C_6H_6}$	$^3J_{C_6H_\alpha}$	$^3J_{C_{1'}H_{3'/5'}}$
(1)^b	127.2				158							
(1)$^{-c}$	147.5				149					152		
(2)^d	130	3.8	7.2	7.2	168.7	4.3	3.4					
(2)$^{-e}$	152.2				159.3							
(3)	132.7		6.4	6.4	174.8	4.3		172.5	4.3	169.3	5.1	7.3
(3)$^{-f}$	160.8	3.5			165.6	3.8	4.1	167.6	5.3	162.7	8.7	7.3
(4)	134.5	4.2	7.0	7.0	175.0	4.5		173.2	4.6	169.4	4.7	
(4)$^-$	164.2	2.8			168.6	3.6		168.8	5.5	165.7	7.6	
(5)	135.8	4.2	5.9	5.9	178.5	5.0	5.0					
(5)$^-$	166.6	3.8			169.1	4.8						
(6)	136.3		5.2		179.1	4.1						
(6)$^-$	163.7		4.2	4.9	172.9	4.6	4.5					

Compd.	$^2J_{C_{1'}H_\alpha}$	$^1J_{C_{2'}H_{2'}}$	$^3J_{C_{2'}H_{6'}}$	$^3J_{C_{2'}H_\alpha}$	$^1J_{C_{3'}H_{3'}}$	$^3J_{C_{3'}H_{5'}}$	$^2J_{C_{4'}H_{3'/5'}}$	$^3J_{C_{4'}H_{2'/6'}}$	$^1J_{C_{5'}H_{5'}}$	$^3J_{C_{5'}H_{3'}}$	$^1J_{C_{6'}H_{6'}}$	$^3J_{C_{6'}H_\alpha}$
(1)^b												
(1)$^{-c}$												
(2)^d												
(2)$^{-e}$												
(3)	7.3	164.0	6.0		169.1	4.2						
(3)$^{-f}$		162.5	6.3	6.3	166.4	4.4	2.8	9.7				
(4)												
(4)$^-$												
(5)					175.2	4.7	4.3	10.2	172.8	4.8	168.9	3.7
(5)$^-$					172.7	5.0			171.5	5.0	161.9	
(6)												
(6)$^-$												

^{a} J/Hz, solvent [$^2H_6$]Me$_2$SO. ^{b} Data taken from ref. 19 and 21. Solvent THF, $^1J_{C_2H_2}$ 158, $^1J_{C_4H_4}$ 160. ^{c} Data taken from refs. 19 and 21. Solvent THF, $M^+ = \mathrm{Li}^+$. $^1J_{C_2H_2}$ 152, $^1J_{C_4H_4}$ 157. ^{d} $^1J_{C_2H_2}$ 163.9. ^{e} $^1J_{C_2H_2}$ 165.8. ^{f} $^3J_{C_4H_6}$ 8.3.

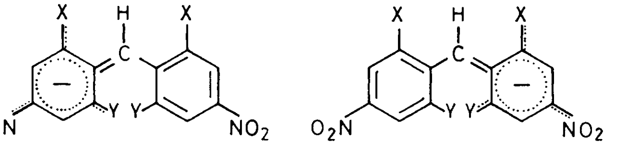
moiety,[29] while the shielding of C(6) was attributed to a γ-effect.[20] It seems reasonable to assume that the changes in chemical shifts due to tri-*o*-nitro substitution have the same origin as those due to tri-*o*-methyl substitution. This, therefore, suggests that tri-*o*-nitro-substituted diphenylmethanes, such as **(5)** adopt, preferentially, the perpendicular conformation (*a*), while the mono- and di-*o*-nitro-substituted analogues, *i.e.* **(3)** and **(4)** exist presumably in the skew conformation (*b*). Due to the lack of *ortho* protons in **(6)**, no conclusion can be drawn as to whether the preferred conformation of hexanitrodiphenylmethane is of type (*a*) or (*b*), but it is to be noted that the tetra-*o*-methyl-substituted analogue exists predominantly in form (*b*).[28]

Table 1 shows that the H_α resonance changes to lower field in the series from **(1)** to **(6)**, in accord with the electron-withdrawing effect of the NO_2 group. In contrast, Table 2 shows that C_α is essentially unaffected by introduction of *para* NO_2 groups but becomes more and more shielded with an increase in the number of *ortho* nitro substituents. These observations are similar to those reported for toluene derivatives[30,31] and there is no doubt that the important *ortho* effect reflects a proximity effect since the nitrogen and oxygen atoms of an *ortho* NO_2 group are in the γ and δ positions relative to C_α respectively.

Despite the complexity of the patterns of some resonances in the proton-coupled ^{13}C spectra, a number of J_{CH} coupling constants could be assigned and the results are given in Table 3. In particular, C_α is coupled not only with the two methylene α-protons but also to available *ortho* protons. This gives rise, for example, to a well-resolved triplet of quintuplets in the spectrum of 4,4′-dinitrodiphenylmethane **(2)**. To be noted is that $^1J_{C_\alpha H_\alpha}$ increases from 127.2 Hz for **(1)**[19] to 136.3 Hz for **(6)**, consistent with increasing the number of electron-withdrawing substituents. On the other hand, the C(1) carbon exhibits a $^3J_{C(1)H(3)/5}$ coupling as well as a $^2J_{C(1)H_\alpha}$ coupling, both of them being equal and in the range 5 to 7 Hz. As a consequence of this equality, C(1) appears as a quintet. A similar situation holds for C(1′) in an unsymmetrical derivative such as **(3)**. These results agree with Shapiro's observations for *para* substituted toluenes.[31] The hydrogen-bearing carbons C(3) [and C(5)] give a doublet of doublets due to $^1J_{C(3)H(3)}$ and $^3J_{C(3)H(5)}$ couplings of *ca.* 175 and 4 Hz, respectively. An unambiguous distinction between C(4) and C(4′) in the pentanitro derivative **(5)** comes from the observed patterns: C(4) gives a triplet due to a $^2J_{C(4)H(3)/(5)}$ coupling of 5 Hz while C(4′) gives a doublet of triplets due to $^3J_{C(4')H(6')}$ and $^2J_{C(4')H(3')/(5')}$ couplings of 10.2 and 4.3 Hz, respectively. A value of 10 Hz is typical for a $^3J_{CH}$ involving an aromatic carbon substituted by an electron-withdrawing group.[31–33]

Structures of the carbanions.—The ^1H and ^{13}C shifts, and the one-bond coupling constant $^1J_{C_\alpha H_\alpha}$ of the carbanionic centre are n.m.r. parameters which are known to be sensitive to the structural reorganization which characterizes the formation of a carbanion.[34] Here, the H_α and C_α resonances suffer very large downfield shifts on ionization of the nitrodiphenylmethanes: the $\Delta\delta_{H_\alpha}$ values lie in the range 1.38–2.72 ppm while those for $\Delta\delta_{C_\alpha}$ lie between 65 and 70 ppm, *i.e.* they are considerably larger than those reported for ionization of diphenylmethane ($\Delta\delta_{H_\alpha}$ 0.25 and $\Delta\delta_{C_\alpha}$ 39 ppm).[19] Although such Δδ values are mainly the result of two opposing effects, namely a high-field shift caused by the presence of the negative charge and a low-field shift caused by the $sp^3 \longrightarrow sp^2$ rehybridization, the importance of the observed down-field variations suggests that the rehybridization factor is predominant. This implies an extensive delocalization of the negative charge and, therefore, that at least one of the aromatic rings of the carbanions lies in the plane of the trigonal C_α carbon.

Unambiguous confirmation that the exocyclic C_α carbon of the nitrocarbanions **(2)**$^-$**(6)**$^-$ is alkene-like comes from the large $^1J_{C_\alpha H_\alpha}$ values which are in the range 152–166 Hz, *i.e.* they are close to values found for sp^2 carbons.[34] Also significant are the variations in these coupling constants brought about by the



(*c*) (*d*)

X = Y = H; X = H, Y = NO$_2$, X = Y = NO$_2$

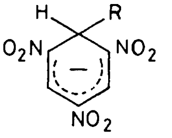
Figure 2.

ionization: the $\Delta^1J_{C_\alpha H_\alpha}$ values range from 22 to 30 Hz. This is compared to a value of 20 Hz for the formation of the unsubstituted carbanion **(1)**$^-$, the exocyclic carbon of which is assumed to be sp^2 hybridized.[8,19,35]

The carbanions with two similarly substituted rings *i.e.* **(2)**$^-$,[36] **(4)**$^-$, and **(6)**$^-$ exhibit only one set of signals for the two aromatic rings in their ^{1}H and ^{13}C spectra at room temperature, confirming the equivalence of structures represented by (*c*) and (*d*) (Figure 2). In addition, there is isochrony of proton and carbon nuclei at the *ortho* and *meta* positions in the symmetrically substituted rings of **(2)**$^-$, **(3)**$^-$, **(5)**$^-$, and **(6)**$^-$. This observation indicates that rotation of these symmetrically substituted rings around the C_α–C_{Ar} bonds of the carbanions is rapid on the n.m.r. time scale at room temperature, as found for their precursors. If rotation of a trinitro-substituted ring occurs in **(6)**$^-$ and **(5)**$^-$, it seems probable that the dinitro-substituted rings in **(5)**$^-$, **(4)**$^-$, and **(3)**$^-$ would also be susceptible to rotation around the corresponding C_α–C_{Ar} bonds. However, due to the unsymmetrical substitution pattern of these rings, n.m.r. spectroscopy cannot provide information on this point. A similar situation holds for the parent molecules.

The ^{1}H n.m.r. spectra have two noteworthy features. The first relates to the chemical shifts for the trinitro- and pentanitrocarbanions **(3)**$^-$ and **(5)**$^-$, which have two phenyl rings bearing different substituents. In these instances, the proton shifts of the less substituted rings are approximately the same as those for the neutral precursors, while those of the more substituted rings suffer strong upfield shifts compared to the starting materials; except for $\delta_{H(3)}$ of **(3)**$^-$. For example, in the 2,4,4′-trinitrodiphenylmethane system **(3)**, the ionization induces a negligible shielding of $H_{(2')/(6')}$ (−0.04 ppm) and a weak shielding of $H_{(3')/(5')}$ (−0.17 ppm) in the mononitro-substituted ring, but it results in shieldings of −0.07, −1.35, and −0.55 ppm for H(3), H(5), and H(6) in the dinitro-substituted ring, respectively. Changes in ^{13}C chemical shifts show a similar trend. This suggests that the ring with greatest substitution plays a dominant role in the delocalization of the negative charge in **(3)**$^-$ and **(5)**$^-$, implying a greater contribution from the mesomeric structures **(3a)**$^-$, **(3b)**$^-$, and **(5a)**$^-$–**(5c)**$^-$ than of those denoted by **(3c)**$^-$ and **(5d)**$^-$, **(5e)**$^-$.

In accord with this idea, the $^3J_{56}$ proton–proton coupling constant for the dinitro ring increases from 8.5 Hz in **(3)** to 10.0 Hz in **(3)**$^-$ while the corresponding N doublet, which gives the sum $^3J_{ortho} + {}^5J_{para}$ for the mononitro ring, remains essentially the same. This shows that the π-bond order of the 5–6 bond increases significantly[37] in the dinitro-substituted ring of **(3)**$^-$, with the major contributing *para*- and *ortho*-quinonoid structures **(3a)**$^-$ and **(3b)**$^-$. For the pentanitrodiphenylmethane system **(5)**, the absence of a proton in the 6-position precludes the observation of a $^3J_{HH}$ coupling in the trinitro-substituted ring, but it is to be noted that the $^3J_{(5')(6')}$ is 8.9 Hz in the dinitrophenyl ring of **(5)**$^-$, close to the value observed in the parent molecule (8.7 Hz). Clearly this supports a predominant charge delocalization into the trinitrophenyl moiety, *i.e.* structures **(5a)**$^-$–**(5c)**$^-$, and may account for the highly shielded quaternary *para* carbon found (see Table 2). This result is reminiscent of those observed in ^{13}C studies of picryl σ-adducts of general structure **(7)** in which the *para* carbon is the most shielded.[38–41]



R = OMe, CH$_2$COMe, and OC$_6$H$_5$, C$_6$H$_4$OH-*p*

(7)

A second noteworthy feature comes from the observation of a long range $^5J_{5\alpha}$ or $^5J_{5'\alpha}$ proton–proton coupling constant in the tri-, tetra-, and penta-nitro carbanions, **(3)**$^-$–**(5)**$^-$. Such a coupling has been shown to be highly stereospecific and typical for a situation where the intervening bonds take up a coplanar zig-zag arrangement.[42,43] In the present case, this type of coupling could only be observed in the dinitroaromatic rings and it ranges from 1.0$_8$ for **(3)**$^-$ to 0.7 for **(4)**$^-$ and, to 0.6 Hz for **(5)**$^-$. These results imply that conformations involving coplanarity of the dinitro-substituted ring with the exocyclic C_α and H_α atoms are notably populated. Furthermore, since this

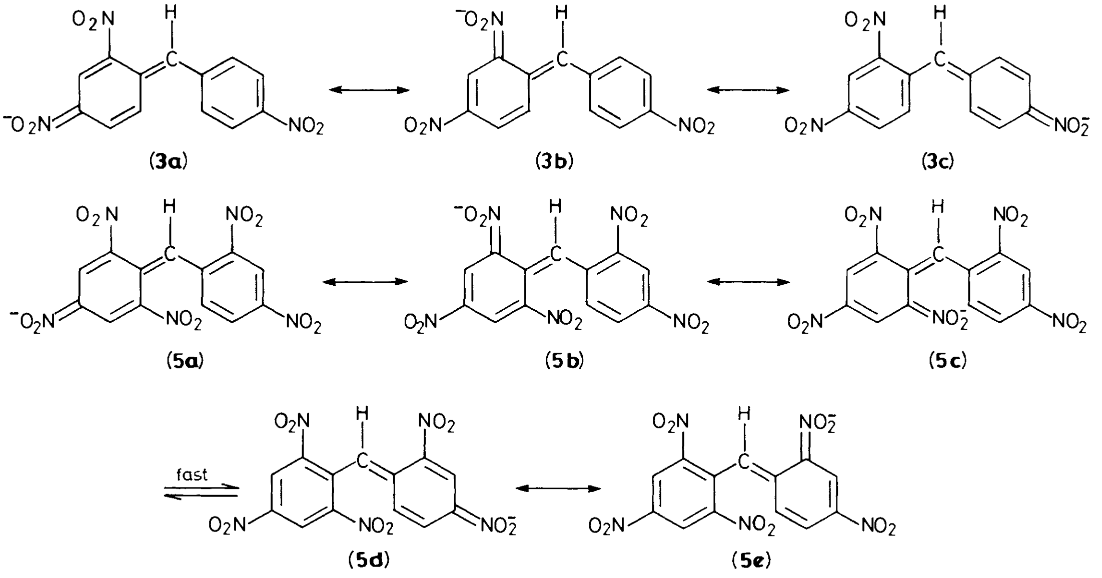


Table 4. Long wavelength absorption bands for nitro-substituted diphenylmethane and toluene anions.[a]

	No. of NO_2 substituents	Substituent positions	λ_{max}/nm	$\varepsilon/10^4$ mol dm^{-3} cm^{-1}
Ar_2CH^-	0		443[b]	4.7[b]
	1	4	520	1.5
	2	4,4′	782	9.7
	3	2,4,4′	692	4.65
	4	2,4,2′,4′	708	5.4
	5	2,4,6,2′,4′	577	2.6
	6	2,4,6,2′,4′,6′	626	2.3
$ArCH_2^-$[c]	1	4	442	1.5
	2	2,4	660, 710	1.4, 0.85[d]
	3	2,4,6	522, 630	1.6, 1.0[d]

[a] Spectra taken at room temperature in 95% Me_2SO–5% MeOH/MeOK solution. [b] Cyclohexylamine solution, ref. 9. See also R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, 1963, **85**, 1651. [c] Values for Me_2SO solution, taken from ref. 46. [d] Calculated from data given in ref. 46.

$^5J_{HH}$ coupling is not known for the 'anti zig-zag' arrangement,[42] this also indicates that the 2-NO_2 group prefers an outer *ortho* position. This coplanarity was expected for the dinitroaromatic ring of **(3)**$^-$ which has been shown to preferentially delocalize the negative charge (see above), and of course was found for the symmetrical tetranitro carbanion **(4)**$^-$. However, the existence of a $^5J_{5\text{-}\alpha}$ coupling constant for **(5)**$^-$ suggests that the contribution of the canonical structures **(5d)**$^-$ and **(5e)**$^-$ is not negligible, even though the negative charge is primarily delocalized in the trinitro-substituted ring. It is difficult to get additional definitive structure information from the observed decrease in the $^5J_{HH}$ coupling in the series **(3)**$^-$–**(5)**$^-$. Such behaviour can have several origins: (*i*) existence of the conformer with the 2- or 2′-NO_2 group in the inner position and H(5) or H(5′) in the outer one, *i.e.* the 'anti-zig-zag' arrangement;[43] (*ii*) slight twisting of the dinitro-substituted ring out of the $C_\alpha H_\alpha$ plane;[44] (*iii*) changes in the length of the C_α–C_1 bond with the increasing number of nitro groups.[45]

All of the above results contribute to the conclusion that there is always effective overlap between the p-orbital of the ionized alpha carbon and the p_π orbitals of one of the aromatic rings of **(2)**$^-$–**(6)**$^-$. However, the question remains as to whether the two aromatic rings can attain coplanarity simultaneously. Examination of molecular models leaves no doubt, as expected, that no mutual coplanarity can be achieved in **(6)**$^-$ and **(5)**$^-$ which have four and three *ortho* NO_2 groups, respectively. In contrast, the models do not provide any clear answer for **(4)**$^-$ which has two mono-*ortho*-substituted aromatic rings. In this instance, a coplanar geometry seems possible only if one assumes that the substituents occupy the outer *ortho* positions and that the central bond angle may change accordingly to reduce the steric hindrance to a minimum.

Examination of the electronic spectra of the carbanions in Me_2SO (95%)–MeOH (5%) solution gives some support to the above suggestions. In Table 4 λ_{max} and ε values are given for the carbanions derived from diphenylmethane and the nitro derivatives studied here, together with data for the corresponding toluene derivatives for comparison. Where more than one long-wavelength band occurs (*e.g.* in the 2,4- and 2,4,6-substituted toluene anions) data for both bands are shown.

The introduction of one nitro group into one of the *para* positions in diphenylmethane increases λ_{max} for the carbanion by *ca.* 80 nm, as expected, whereas the introduction of a second *para* nitro group causes a much greater bathochromic shift, and increases the extinction coefficient (see Table 4). These observations clearly support extensive participation of both nitro groups in the charge delocalization/conjugation, and suggest the mutual coplanarity of the two aromatic rings in **(2)**$^-$ (and thus also in **(1)**$^-$ and its mononitrated derivative).

Addition of an *ortho* nitro group to **(2)**$^-$ to give **(3)**$^-$ results in a hypsochromic shift and a decrease in ε (see Table 4). This behaviour may be compared with the effect of adding an *ortho* nitro group to the 4-nitrotoluene anion, which results in a large bathochromic shift and a decrease in ε, for the long-wavelength band.[46] The greater possible charge-delocalization in the 2,4-dinitrotoluene anion would lower the energy of the excited state, relative to the ground state, and thus the observed bathochromic shift could be anticipated, and similar behaviour might be expected for **(3)**$^-$. If, however, the bulk of the charge in **(3)**$^-$ is delocalized onto the di- rather than the mono-substituted ring, as suggested by the n.m.r. data discussed above, then this carbanion may be considered to be an α-substituted 2,4-dinitrotoluene anion. Substitution of hydrogen by an electron-withdrawing group at the exocyclic carbon of the 2,4-dinitrotoluene anion should lead to a hypsochromic shift according to Dewar's rules, as is observed (Table 4), the larger extinction coefficient for **(3)**$^-$ suggests that interaction with the *para* nitrophenyl substituent is increased to a maximum and thus the two rings are mutually coplanar. Comparison of **(4)**$^-$ with **(3)**$^-$ shows that the additional *ortho* nitro group has caused a slight increase in both λ_{max} and ε, and that **(4)**$^-$ possesses an absorption maximum at virtually the same wavelength (708 nm) as does the 2,4-dinitrotoluene anion (710 nm). The extinction coefficient for this band of **(4)**$^-$ is *ca.* 6 times that of the corresponding 2,4-dinitrotoluene anion band, the most intense absorption for this latter species occurs at shorter wavelength (660 nm). **(4)**$^-$ may be considered to be the symmetric α-(2,4-dinitrophenyl)-substituted 2,4-dinitrophenylmethyl anion, and as such might be expected to absorb at a wavelength similar to that of the 2,4-dinitrotoluene anion, and with higher ε if the rings are coplanar. Thus, electronic spectroscopic data suggest that this planar arrangement exists in **(4)**$^-$ with the two *ortho* nitro substituents on the outer sides of aromatic rings or that, if ring twisting occurs it is sufficiently low so as to ensure an appreciable conjugation between the two aromatic rings. Recent measurements of the intrinsic reactivities, in the Marcus sense, of the two carbanions support this latter situation: log k_0 − 1.10 and −0.60 for ionization of **(3)** and **(4)**, respectively, by carboxylate ions in 50% H_2O–50% Me_2SO.[13] In keeping with the commonly accepted view that the intrinsic reactivity of carbon acids is primarily a measure of the extent of structural–electronic–solvational reorganization required for carbanion formation,[6,12,14,15,46] the low k_0 values found for **(3)**$^-$ and **(4)**$^-$ indicate that both carbanions have high energy of reorganization. This implies an important delocalization of the negative charge over the two phenyl rings in **(3)**$^-$ and **(4)**$^-$ and therefore an almost planar arrangement. In this regard it is noteworthy that the log k_0 value is slightly higher for **(4)**$^-$ than for **(3)**$^-$, consistent with a somewhat less effective conjugation in the former. This conclusion will also account for the observed $^5J_{HH}$ being less for **(4)**$^-$ than for **(3)**$^-$.

The replacement of one or both of the remaining *ortho* hydrogens of **(4)**$^-$ by nitro groups gives rise to **(5)**$^-$ and **(6)**$^-$, whose λ_{max} values occur at considerably shorter wavelengths (577 and 626 nm, respectively) with lower extinction coefficients than for **(4)**$^-$. A similar shift to shorter wavelength is found when comparing the 2,4,6-trinitro- with the 2,4-dinitrotoluene anion. While a hypsochromic shift is not *per se* evidence of a steric effect, when combined with a significant reduction in the value of ε (*ca.* one half—see Table 4) it is a strong indication of this. The observed behaviour is consistent with structures for **(5)**$^-$ and **(6)**$^-$ in which no mutual coplanarity of the two rings occurs. This is in accord with the n.m.r data which indicate preferential (though not exclusive—see above) charge delocali-

Table 5. Calculated and experimental ^{13}C chemical shifts for symmetrical molecules (**2**), (**4**), and (**6**).

Compound		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
(**2**)	δ_{calc}	146.8	129.5	123.0	145.3		
	δ_{exp}	147.8	130.0	123.6	146.2		
(**4**)	δ_{calc}	141.5	149.1	117.7	146.1	129.0	130.3
	δ_{exp}	139.6	148.6	120.3	146.6	127.7	133.7
(**6**)	δ_{calc}	136.2	149.9	123.7	146.9		
	δ_{exp}	129.4	150.4	123.6	146.8		

zation onto the picryl ring in the (**5**)$^-$ anion. Presumably the symmetry of (**6**)$^-$ gives rise to its absorption at longer wavelength than does (**5**)$^-$. The ε value for (**6**)$^-$ is *ca.* twice that for the 630 nm band of the 2,4,6-trinitrotoluene anion, as expected if the two rings of (**6**)$^-$ are approximately orthogonal.

Experimental

Materials.—All nitrodiphenylmethanes studied were synthesized according to standard procedures. 2,2′,4,4′,6,6′-hexanitrodiphenylmethane, m.p. 231 °C (lit.,[22] m.p. 232 °C); 2,2′,4,4′,6-pentanitrodiphenylmethane, m.p. 209–211 °C (lit.,[22] 208–210 °C); 2,2′,4,4′-tetranitrodiphenylmethane, m.p. 179 °C (lit.,[47] 176 °C); 2,4,4′-trinitrodiphenylmethane, m.p. 111 °C (lit.,[48] 110–111 °C); 4,4′-dinitrodiphenylmethane, m.p. 181 °C (lit.,[49] 181–182 °C).

N.M.R. and U.V.–Visible Measurements.—N.m.r. spectra were recorded on a Bruker AM 250 spectrometer equipped with an ASPECT 3000 Computer, using the F.T. mode. Chemical shifts were measured relative to the solvent [$^2H_6$]DMSO and converted into the TMS scale (δ_H 2.50; δ_C 39.5).

The various diphenylmethanes were dissolved in [$^2H_6$]-DMSO (conc. *ca.* 0.2 mol dm^{-3}) and the carbanions were generated *in situ* by adding an equimolar amount of methanolic potassium methoxide (*ca.* 5.5 mol dm^{-3}) to the above solutions. Under these experimental conditions, the stability of the diphenylmethyl carbanions was generally sufficient as to provide well-resolved ^1H and noise proton-decoupled ^{13}C spectra. In contrast, proton-coupled ^{13}C spectra which require longer acquisition times were sometimes less satisfactory reflecting the slow decomposition of the carbanions in basic media.

Experimental ^{13}C chemical shifts for symmetrical molecules (**2**), (**3**), and (**6**) are compared in Table 5 with those calculated using Buchanan's values for diphenylmethane[20] and Breitmaier's NO_2 increments.[24,25] (Z_o −5.3, Z_m +0.8, Z_p +6.0, Z_i +19.6 ppm).

U.v.–visible spectra of the carbanions were recorded in DMSO (95%)–MeOH (5%) with concentrations in the range $3\text{–}5 \times 10^{-5}$ mol dm^{-3}. A conventional Shimadzu UV-160 spectrophotometer was used for (**2**)$^-$ to (**6**)$^-$ while a Durrum–Gibson stopped-flow spectrophotometer was employed for the less stable 4-nitrodiphenylmethyl carbanion.

Acknowledgements

The authors are very grateful to Marie-José Pouet for recording the n.m.r. spectra.

References

1 J. R. Jones, 'The Ionization of Carbon Acids,' Academic Press, London and New York, 1971.
2 F. G. Bordwell, *Pure Appl. Chem.*, 1977, **49**, 863.
3 A. Streitwieser, Jr., E. Juaristi, and L. Nebenzahl, in 'Comprehensive Carbanion Chemistry,' eds. E. Buncel and T. Durst, Elsevier, Amsterdam, 1980, p. 323.
4 F. G. Bordwell, J. E. Bartmess, and J. A. Hautala, *J. Org. Chem.*, 1978, **43**, 3107 and 3113 and references cited therein.
5 C. F. Bernasconi and S. A. Hibdon, *J. Am. Chem. Soc.*, 1983, **105**, 4343.
6 C. F. Bernasconi, *Pure Appl. Chem.*, 1982, **54**, 2335.
7 V. R. Sandel and H. H. Freedman, *J. Am. Chem. Soc.*, 1963, **85**, 2328.
8 R. Waack, M. A. Doran, E. B. Baker, and G. A. Olah, *J. Am. Chem. Soc.*, 1966, **88**, 1272.
9 S. M. Adams and S. Bank, *J. Comput. Chem.*, 1983, **4**, 470 and references therein.
10 S. Bank, J. Sturges, and C. H. Bushweller, in 'Stereodynamics of Molecular Systems,' R. H. Sarma, ed., Pergamon, New York, 1979, p. 147.
11 C. F. Bernasconi and R. D. Bunnell, *Isr. J. Chem.*, 1985, **26**, 420.
12 C. F. Bernasconi, *Tetrahedron*, 1985, **41**, 3219.
13 F. Terrier, J. Lelievre, A.P. Chatrousse, and R. Schaal, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1479.
14 C. F. Bernasconi and P. Paschalis, *J. Am. Chem. Soc.*, 1986, **108**, 2969.
15 C. F. Bernasconi and F. Terrier, *J. Am. Chem. Soc.*, 1987, **109**, 7115.
16 J. P. L. Cox, M. R. Crampton, and P. Wight, *J. Chem. Soc., Perkin Trans. 2*, 1988, 25.
17 J. W. Bunting and D. Stefanidis, *J. Am. Chem. Soc.*, 1988, **110**, 4008.
18 C. F. Bernasconi, R. D. Bunnell, and F. Terrier, *J. Am. Chem. Soc.*, 1988, **110**, 6514.
19 S. Bradamante and G. A. Pagani, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1035.
20 G. W. Buchanan, G. Montaudo, and P. Finocchiaro, *Can. J. Chem.*, 1974, **52**, 3196.
21 J. P. C. M. Van Dongen, H. W. D. Van Dijkman, and M. J. A. de Bie, *Rec. Trav. Chim. Pays-Bas*, 1974, **93**, 30.
22 K. G. Shipp, L. A. Kaplan, and M. E. Sitzmann, *J. Org. Chem.*, 1972, **37**, 1966.
23 G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Am. Chem. Soc.*, 1972, **94**, 3089.
24 B. E. Breitmaier and G. Bauer, *Pharm. Unserer Zeit.*, 1976, **5**, 97.
25 K. A. Kovar and E. Breitmaier, *Chem. Ber.*, 1978, **111**, 1646.
26 E. J. W. Whittaker, *Acra Crystallogr.*, 1953, **6**, 714.
27 M. J. Housty, *Acta Crystallogr.*, 1961, **14**, 92.
28 G. Montaudo, S. Caccamese, and P. Finocchiaro, *J. Am. Chem. Soc.*, 1971, **93**, 4202.
29 C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.
30 W. B. Smith and T. W. Proulx, *Org. Magn. Reson.*, 1976, **8**, 567.
31 M. J. Shapiro, *J. Org. Chem.*, 1978, **43**, 212.
32 A. R. Tarpley and J. H. Goldstein, *J. Mol. Spectrosc.*, 1971, **39**, 275.
33 A. R. Tarpley and J. H. Goldstein, *J. Phys. Chem.*, 1972, **76**, 515.
34 J. P. Stothers, 'Carbon-13 N.M.R. Spectroscopy,' Academic Press, 1972, p. 210.
35 H. McNab, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1287.
36 C. A. Fyfe, A. Albagli, and R. Stewart, *Can. J. Chem.*, 1970, **48**, 3721.
37 K. D. Bartle, D. W. Jones, and R. S. Matthews, *J. Mol. Struct.*, 1969, **4**, 445 and references therein.
38 G. A. Olah and H. Mayr, *J. Org. Chem.*, 1976, **41**, 3448.
39 R. A. Renfrow, M. J. Strauss, and F. Terrier, *J. Org. Chem.*, 1980, **45**, 471.
40 J. A. Chudek, R. Foster, and A. W. Marr, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1341.
41 V. Machacek, V. Sterda, A. Lycha, and D. Snobl, *J. Chem. Soc., Perkin Trans. 2*, 1982, 355.
42 R. Wasylishen and T. Schaefer, *Can. J. Chem.*, 1971, **49**, 3216.
43 W. Danchura, T. Schaefer, J. B. Rowbotham, and D. J. Wood, *Can. J. Chem.*, 1974, **52**, 3986.
44 J. B. Rowbotham, A. F. Janzen, J. Peeling, and T. Schaefer, *Can. J. Chem.*, 1974, **52**, 481.
45 W. F. Reynolds, I. R. Peat, and G. K. Hamer, *Can. J. Chem.*, 1974, **52**, 3415.
46 E. Buncel, T. K. Venkatachalam, and B. C. Menon, *J. Org. Chem.*, 1984, **49**, 413.
47 G. D. Parkes and R. H. H. Morley, *J. Chem. Soc.*, 1936, 1478.
48 A. L. Bluhm, J. A. Sousa, and J. Weinstein, *J. Org. Chem.*, 1964, **29**, 636.
49 K. Bowden and R. Stewart, *Tetrahedron*, 1965, **21**, 261.

Received 4*th January* 1989; *Paper* 9/00045C