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BOND LENGTHS IN BENZENE DERIVATIVES

HYBRIDIZATION OR RESONANCE

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Abstract—The measured bond lengths in nitrobenzene and in other simple benzene derivatives indicate that there is little or no resonance involving excited structures. The bond length variations can however be explained by differences in hybridization of the carbon σ orbitals.

INTRODUCTION

The shortening of C–C bond lengths (in comparison with the usual single bond distance) in conjugated or hyperconjugated molecules, such as butadiene or propylene, is generally attributed to the effects of π-electron resonance. Recently Dewar and Schmeising[1] have questioned the interpretation of the evidence for the existence of appreciable π-electron resonance in the ground states of conjugated or hyperconjugated molecules, and have concluded that all observed effects are explainable as a result of differences in hybridization of carbon σ orbitals, resonance effects being negligible. They suggest that resonance is important only in those molecules, such as benzene, where more than one classical (unexcited) structure can be written, but that even in these cases the effects of π-electron resonance are much smaller than is usually believed.

Mulliken[2] has further examined this problem and has concluded that, while Dewar and Schmeising are partly right in suggesting that the lengths of conjugated and hyperconjugated C–C bonds are determined, to a greater extent than is usually supposed, by the states of hybridization of the carbon bond orbitals rather than by π-electron resonance, there seems to be no justification for the assumption that the π-delocalization shortenings are negligible. He has analysed the C–C bond length shortenings in several conjugated and hyperconjugated molecules, and has attributed 40 per cent of the observed shortenings to π-electron resonance, and 60 per cent to hybridization differences.

We have recently completed a detailed X-ray analysis of the crystal and molecular structure of nitrobenzene at $-30°$,[3] and the measured bond lengths and valency angles provide some additional information on the problem of the relative importance of resonance and of hybridization differences. One difficulty in estimating the value of the evidence provided by the measured dimensions of the nitrobenzene molecule is that the accuracy of the results obtained by X-ray diffraction of crystals is not nearly as good as that given by spectroscopic methods, although of course the X-ray method has the advantage of being able to deal with more complex molecules. The estimated standard deviations of the carbon–carbon bond lengths in nitrobenzene,

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[1] M. J. S. Dewar and A. N. Schmeising, *Tetrahedron* **5**, 166 (1959).

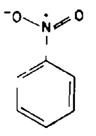
[2] R. S. Mulliken, *Tetrahedron* **6**, 68 (1959).

[3] J. Trotter, *Acta Cryst.* **12**, 884 (1959).

for example, are 0·014 Å, while the spectroscopic method for simpler molecules gives an accuracy of the order of 0·001 Å. We did not therefore feel justified in basing our conclusions only on the results of the investigation of the nitrobenzene structure, and we also examined the results of X-ray investigations of other mono-substituted benzenes reported in the literature.

NITROBENZENE

Resonance theory predicts that in nitrobenzene (I), as in other simple benzene derivatives, contributions to the ground state of the molecule from ionic (excited) structures such as II and III decrease the length of the C–N bond, in comparison with the corresponding distance in a non-conjugated molecule, and in addition lead to variations of the carbon–carbon bond lengths from the distances in benzene, such that bonds 1–2 and 1–6 are the longest and 2–3 and 5–6 the shortest in the aromatic ring. Calculations by molecular orbital methods show that the variations to be expected in carbon–carbon bond lengths are quite small; for nitrobenzene, for example, a simple calculation[4] shows that the predicted lengths of the bonds 1–2, 2–3, 3–4 are 1·399 1·392, 1·394 Å respectively. The predicted shortening of the C–N bond is much greater than these rather small variations, although it is difficult to make an exact estimate because of uncertainties in the bond order-bond length correlation curve in the range of bond orders involved.[4]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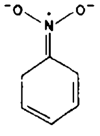
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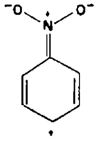
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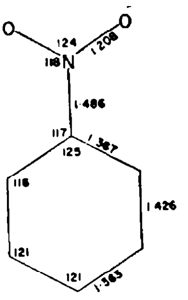

FIG. 1. Bond lengths (Å) and valency angles (degrees) in nitrobenzene.

The X-ray analysis of the crystal and molecular structure of nitrobenzene at —30° revealed that the molecule was completely planar with symmetry *mm*2 (we did not feel at the outset of the analysis that this would necessarily be so, as the *p*-dinitrobenzene molecule, for example, has been shown to be slightly non-planar,[5] at least in the solid state); the bond lengths and valency angles in the nitrobenzene molecule are shown in Fig. 1. The values of the bond distances indicate, firstly that the variations in the lengths of carbon–carbon bonds are much larger than predicted by resonance

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[4] J. Trotter, *Canad. J. Chem.* 37, 905 (1959).
[5] S. C. Abrahams, *Acta Cryst.* 3, 194 (1950).

theory, and in addition in the wrong direction, bonds 2–3 and 5–6 being significantly longer than the other aromatic bonds; and secondly that the C–N bond is not shortened in comparison with the corresponding bond in a non-conjugated molecule and indeed it is a little longer than the value usually quoted for the C–N single bond distance (1·475 Å). These points will be discussed in turn.

C–C bond lengths

The estimated standard deviations of the measured carbon–carbon bond lengths in nitrobenzene are 0·014 Å, so that bond 1–2 does not differ significantly in length from bond 3–4, but bond 2–3 is very significantly longer (0·06 Å) than the other two chemically-independent carbon-carbon bonds in the aromatic ring. These bond length variations are in the opposite direction to those predicted by resonance theory, and suggest that changes in the hybridization of the aromatic carbon atoms from those in benzene result in changes in the carbon–carbon bond lengths which are much larger than any variations due to π-electron resonance. We have not carried out any elaborate calculations, but some quite simple considerations indicate that the bond length variations can be explained on the basis of changes in carbon atom hybridizations. It would be expected that an increase in the valency angle in the aromatic ring at one of the carbon atoms would shorten the aromatic bonds involving that atom, since there is an increase in the s character of the hybrid orbitals, and conversely a decrease in valency angle would increase the bond lengths. Taking the carbon–carbon bond lengths in benzene as 1·392 Å (the value determined by X-ray diffraction methods), the covalent radius of a carbon atom in benzene is 0·696 Å. Utilizing the measured bond lengths in nitrobenzene, and taking $r_3 = r_4$ since the angles at these atoms are equal, we obtain for the effective covalent radii of the carbon atoms in the aromatic bonds:

$$r_1 = 0{\cdot}623 \text{ Å}$$

$$r_2 = 0{\cdot}744$$

$$r_3 = 0{\cdot}682$$

$$r_4 = 0{\cdot}682$$

An approximately linear correlation may then be established between valency angle and effective covalent radius (Fig. 2), which of course gives an adequate account of the dimensions of the aromatic ring in the nitrobenzene molecule (Table 1). This procedure is approximately equivalent to using the expressions given by Coulson[6] for the hybridization ratio, λ, in a hybrid orbital.

The validity of this correlation may be judged by using the method for predicting bond length variations in other molecules. We applied Fig. 2 to the calculation of the type of bond length variation to be expected in nitromesitylene. The valency angles in the aromatic ring (Fig. 3), determined by X-ray analysis of the crystalline material,[7] differ by greater amounts from the 120° in benzene than do the angles in the nitrobenzene molecule. These larger deviations are probably the result of steric effects which twist the nitro group about the C–N bond 66° out of the aromatic plane. Using

[6] C. A. Coulson, *V. Henri Memorial Volume* p. 15. Desoer, Liége (1948).

[7] J. Trotter, *Acta Cryst.* **12**, 605 (1959).

TABLE 1. MEASURED AND CALCULATED BOND LENGTHS (Å)

Molecule	Bond	Measured length	Length calculated from Fig. 2.
Nitrobenzene	1–2	1·37	1·38
	2–3	1·43	1·43
	3–4	1·36	1·37
Nitromesitylene	1–2	1·37	1·37
	2–3	1·41*	1·43
	3–4	1·37	1·38

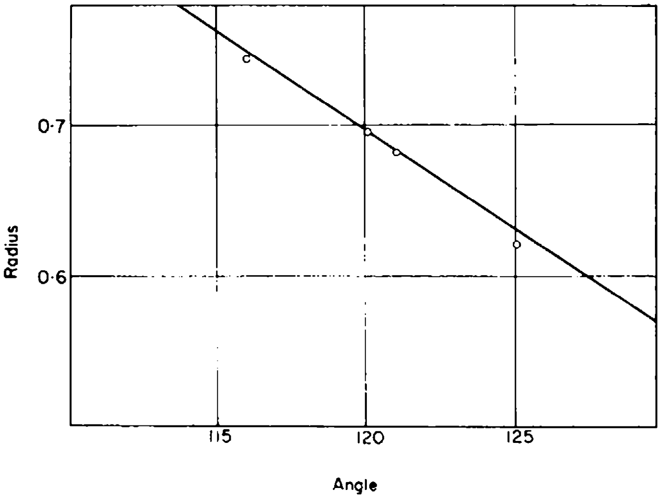

FIG. 2. Effective covalent radius as a function of valency angle.

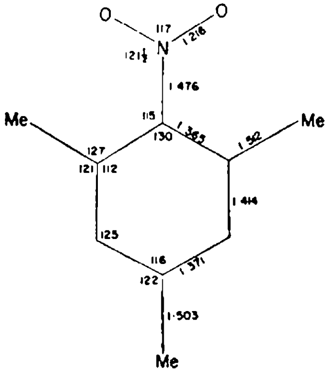

FIG. 3. Bond lengths (Å) and valency angles (degrees) in nitromesitylene.

the measured valency angles, the effective atomic radii of the aromatic carbon atoms, determined from Fig. 2, are:

$$r_1 = 0{\cdot}564\ \text{Å}$$

$$r_2 = 0{\cdot}803$$

$$r_3 = 0{\cdot}630$$

$$r_4 = 0{\cdot}750$$

The corresponding values of the aromatic carbon–carbon bond lengths are compared in Table 1 with the measured values, and the agreement is reasonably good considering the accuracy of the measured values and the rather approximate method for estimating the calculated values.

It would appear then that it is reasonable to ascribe the aromatic bond length variations in nitrobenzene and nitromesitylene to changes in hybridization of the carbon σ orbitals from those in benzene, and that the rather approximate method suggested for allowing for these differences in hybridization gives quite good agreement with the observed effects. We would not expect Fig. 2 to be accurately applicable to other benzene derivatives, since the bond lengths used in deriving it have been measured with limited accuracy, but some correlation of this type may be useful for other molecules.

Although the C–C bond length variations can be correlated with the changes in hybridization, it is not immediately apparent why such differences in valency angle should occur. One possible explanation is the steric effect of the substituent nitro group on the *ortho* hydrogen atoms in nitrobenzene. That this is a reasonable explanation is supported by the rather larger differences in valency angles in nitromesitylene, where the methyl groups produce considerable steric strain in the molecule and indeed cause significant deviations from coplanarity. It is possible also of course that intermolecular forces in the crystal have a small effect.

Although we can ascribe all the variations in the carbon–carbon bond lengths to hybridization differences, this does not in itself necessarily imply that π-electron resonance (apart from that in benzene and the nitro group separately) is negligible, since the bond length variations predicted by resonance theory would probably be too small to be observed accurately by X-ray diffraction methods, even if they could be separated from the hybridization effects. The C–N bond distance, for which resonance theory predicts a considerable shortening, ought to yield more information about the relative magnitudes of resonance and hybridization in nitrobenzene.

C–N bond length

The derivation of C–N bond lengths in aromatic nitro compounds by molecular orbital methods is complicated by uncertainties in the bond order bond length correlation curve in the range of bond orders involved.[4] Two different and equally plausible correlation curves give values of 1·39 Å and 1·43 Å for the calculated carbon–nitrogen bond distance in nitrobenzene.

Calculations by the molecular orbital method[4] show that resonance increases the bond order of the C_2–C_3 bond in nitrobenzene from 0·667 to 0·675, but the order of the C–N bond from 0 to 0·322; apart then from possible differences in the forms of the C–C and C–N order–length correlation curves in the regions of bond order involved, we should expect the shortening of the C–N bond to be about 40 times that of the C_2–C_3 bond, that is about 0·04 Å.

The value usually quoted for the C–N bond length in nitromethane is 1·47 Å, although a value of 1·49 Å has recently been given.[8] For aromatic nitro compounds values as low as 1·35 Å have been reported for picryl iodide[9] and 1:5-dinitronaphthalene,[10] although for the latter molecule a recent redetermination of the crystal structure[11] has shown that the C–N distance is actually 1·486 Å—identical with the corresponding distance in nitrobenzene. For *m*-dinitrobenzene values as far apart as 1·39 Å and 1·54 Å have been reported in different investigations,[12,13] while the C–N bond length in *p*-dinitrobenzene[5] has been measured as 1·48 Å.

It is probably more useful to compare the C–N bond length in nitrobenzene (1·486 Å) with the lengths in aromatic nitro compounds in which any resonance interaction between the nitro group and the aromatic rings is reduced by some means. In nitromesitylene the steric effects of neighbouring carbon and hydrogen atoms prevent the nitro group from being coplanar with the plane of the aromatic rings, and X-ray analysis[7] has shown that the NO_2 group is rotated about the C–N bond 66° out of the aromatic plane, the C–N distance being 1·48 Å; the twist of 66° implies that resonance interaction across the C–N bond is only about 0·17 ($\cos^2 66°$) of that in a coplanar structure. In 9-nitroanthracene[14] similar steric effects twist the nitro group 85° out of the anthracene plane, so that the C–N bond length in this molecule (1·48 Å) may be taken as the distance in a non-conjugated nitro compound with a trigonal carbon atom. The measured carbon–nitrogen bond distance in nitrobenzene suggests that, if there is any shortening as the result of resonance interaction, it is more or less balanced by a lengthening due to differences in hybridization of the carbon and nitrogen atoms in nitrobenzene and in 9-nitroanthracene. However the exocyclic valency angles in nitrobenzene are identical with those in 9-nitroanthracene, so that the hybridization effects should be the same for the C–N bonds in both molecules. The apparent reasonable conclusion is that any resonance interaction across the C–N bond in nitrobenzene is insufficient to cause any measurable shortening of the bond distance.

We would prefer not to be too dogmatic about this conclusion, since the accuracy of the X-ray results does not definitely exclude, for any one molecule, the possibility of the non-observance of a shortening of the C–N bond being due to experimental error. Nevertheless in none of the nitro compounds we have studied is the C–N distance (these are summarized in Table 2) significantly shorter than 1·48 Å. Indeed only for 9:10-dinitroanthracene[15] is the difference as great as 0·03 Å, and the accuracy of that particular analysis is such that this is still only possibly significantly less than 1·48 Å.

It appears then that in nitrobenzene the measured lengths of the C–C and C–N bonds indicate no variations and shortenings such as are predicted by resonance theory.

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[8] *Tables of Interatomic Distances and Configurations in Molecules and Ions.* Chemical Society Special Publication No. 11, London (1958).

[9] G. Huse and H. M. Powell, *J. Chem. Soc.* 1398 (1940).

[10] N. G. Sevastyanov, G. S. Zhdanov and M. M. Umansky, *J. Phys. Chem. Russ.* **22**, 1153 (1948).

[11] J. Trotter, *Acta Cryst.* In press.

[12] N. W. Gregory and E. N. Lassettre, *J. Amer. Chem. Soc.* **69**, 102 (1947).

[13] E. M. Archer, *Proc. Roy. Soc.* A **188**, 51 (1946).

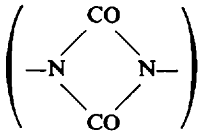
[14] J. Trotter, *Acta Cryst.* **12**, 237 (1959).

[15] J. Trotter, *Acta Cryst.* **12**, 232 (1959).

TABLE 2. C–N BOND LENGTHS

Molecule	Nitro group twist	C–N distance
Nitrobenzene	0°	1·49 Å
1:5-Dinitronaphthalene	49	1·49
9:10-Dinitroanthracene	64	1·45
Nitromesitylene	66	1·48
9-Nitroanthracene	85	1·48

TABLE 3. BOND LENGTHS IN BENZENE DERIVATIVES (Å)

Molecule	Aromatic bonds			Exocyclic bonds		
	1–2	2–3	3–4	C–C	C–N	
Benzene[16]	1·39	1·39	1·39	—	—	
Dibenzyl[17]	1·37	1·39	1·37	1·52	—	
Nitrobenzene[8]	1·37	1·43	1·36	—	1·49	(—NO_2)
Nitromesitylene[7]	1·37	1·41	1·37	—	1·48	(—NO_2)
Benzoic acid[18]	1·39	1·41	1·36	1·48	—	
Acetanilide[19]	1·38	1·40	1·39	—	1·43	(—NH·$COCH_3$)
Phenyl isocyanate dimer[20]	1·35	1·39	1·37	—	1·41	
KH Dibenzoate[21]	1·37	1·40	1·37	1·53	—	
Ephedrine hydrochloride[22]	1·37	1·44	1·36	1·56	—	
p-Toluidine hydrochloride[23]	1·38	1·42	1·39	—	1·45	(—NH_3)
Mean	$1{\cdot}37_2$	$1{\cdot}41_0$	$1{\cdot}37_1$			

OTHER BENZENE DERIVATIVES

As we pointed out in the introduction we do not feel justified in basing our conclusions only on the analysis of the crystal structures of nitrobenzene and nitromesitylene, and we have collected in Table 3 the measured bond lengths in most of the monosubstituted benzene derivatives which have been examined reasonably accurately by the X-ray method (nitromesitylene and *p*-toluidine hydrochloride have methyl substituents in addition to the functional group). These data were taken chiefly from *Tables of Interatomic Distances*.[8] In a few of the investigations reported in the literature the measured aromatic bond lengths do not differ significantly from

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[16] E. G. Cox, D. W. J. Cruickshank and J. A. S. Smith, *Proc. Roy. Soc.* A **247**, 1 (1958).
[17] D. W. J. Cruickshank, *Acta Cryst.* **2**, 65 (1949).
[18] G. A. Sim, J. M. Robertson and T. H. Goodwin, *Acta Cryst.* **8**, 157 (1955).
[19] C. J. Brown and D. E. C. Corbridge, *Acta Cryst.* **7**, 711 (1954).
[20] C. J. Brown, *J. Chem. Soc.* 2931 (1955).
[21] J. M. Skinner, G. Stewart and J. C. Speakman, *J. Chem. Soc.* 180 (1954).
[22] D. C. Phillips, *Acta Cryst.* **7**, 159 (1954).
[23] G. von Eller, *Bull. Soc. Fr. Min. Crist.* **78**, 257 (1955).

the mean value, and we have not listed any of these; and in a few cases bond length variations are more or less haphazard. In all the molecules listed in Table 3 (except perhaps acetanilide) we are justified in assuming that the symmetry of the aromatic ring does not differ significantly from *mm*2.

In all of these more accurate structure investigations the variations of the aromatic bond lengths are much larger than and in the opposite direction to those predicted by resonance theory, the mean values of the lengths of bonds 1–2, 2–3 and 3–4 being $1{\cdot}37_2$, $1{\cdot}41_0$, $1{\cdot}37_1$ Å respectively. The valency angles in the aromatic rings in all the molecules in Table 3 are listed in Table 4. The mean values were used to obtain from Fig. 2 the mean values of the effective covalent radii of the aromatic carbon atoms:

TABLE 4. BOND ANGLES IN BENZENE DERIVATIVES (DEGREES)

Molecule	Angles			
	1	2	3	4
Benzene	120	120	120	120
Dibenzyl	—	—	—	—
Nitrobenzene	125	116	121	121
Nitromesitylene	130	112	125	116
Benzoic acid	119	119	122	118
Acetanilide	121	119	120	120
Phenyl isocyanate dimer	120	120	121	118
KH Dibenzoate	—	—	—	—
Ephedrine hydrochloride	123	118	120	121
p-Toluidine hydrochloride	121	119	121	119
Mean	$122{\cdot}_7$	$117{\cdot}_8$	$121{\cdot}_4$	$119{\cdot}_0$

$$r_1 = 0{\cdot}660 \text{ Å}$$

$$r_2 = 0{\cdot}728$$

$$r_3 = 0{\cdot}677$$

$$r_4 = 0{\cdot}710$$

The corresponding calculated values of the aromatic bond lengths are 1–2 = 1·388 Å, 2–3 = 1·405 Å, 3–4 = 1·387 Å, in reasonable agreement with the measured values. The correlation in Fig. 2 has of course been derived from the nitrobenzene results only, and a slightly different straight line would give better overall agreement between measured and calculated bond lengths for all the molecules.

It must be emphasized that the data in Tables 3 and 4 are subject to appreciable and varying uncertainties. The standard deviations of the individual bond lengths for the first seven molecules listed are of the order of 0·01 Å, so that only bond length differences greater than about 0·03–0·04 Å are really significant for any individual molecule. For the last three molecules the possible errors are even greater.

Although for any individual molecule then it would be unwise to draw any definite conclusions from the measured bond length variations (for benzoic acid for example

Goodwin[24] points out that the bond length variations are definitely in the opposite direction to those predicted by resonance theory, but that an accurate three-dimensional analysis may perhaps alter this conclusion) the accumulation of evidence from all the molecules listed supports overwhelmingly the view that no variations in the aromatic carbon–carbon bonds due to resonance are observed, but that hydridization differences result in significant variations of the bond lengths.

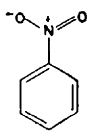
No detailed discussion of the exocyclic bond lengths will be attempted (except for that given above for C–N bonds in nitro compounds) since the substituent groups vary widely.

It is instructive though to compare the C–N distances in nitro compounds, where any resonance would be theoretically of the weakest type (dative and sacrificial), with the corresponding bond lengths in molecules such as aniline, where the resonance is dative isovalent and is therefore expected to be much stronger than in nitrobenzene. Examination of Table 3 indicates that the C–N distances in molecules with dative isovalent conjugation are about 1·43 Å, considerably shorter than the corresponding distances in nitro compounds. Unfortunately there is not a whole series of molecules of this type where we would expect differences in the resonance interaction (as for the nitro compounds listed in Table 2), but the measured distances available do suggest that the C–N bonds are shortened by resonance. In *p*-nitroaniline (which is not included in Table 3, since there are two functional groups) the bond lengths are $\mathrm{C{-}NO_2} = 1{\cdot}41$ Å, $\mathrm{C{-}NH_2} = 1{\cdot}37$ Å.[25] Further accurate measurements of the bond lengths in amines are required before more definite conclusions can be drawn.

FURTHER CONSIDERATIONS

The aromatic carbon–carbon bond lengths in nitrobenzene and other simple benzene derivatives indicate then that no variations due to resonance involving ionic (excited) structures are observed, but that differences in the hybridization of the carbon σ orbitals from those in benzene produce considerable variations in the C–C bond lengths. In all the aromatic nitro compounds which we have investigated by the X-ray method, no shortenings in the C–N distances in comparison with-non-conjugated molecules, such as are predicted by resonance theory, have been observed.

Both these lines of evidence suggest that in the ground state resonance involving excited structures is negligible—in agreement with the conclusion reached by Dewar and Schmeising.[1] The ground state of the nitrobenzene molecule can be represented as a resonance hybrid of the structures IV–VII. The measured bond lengths also



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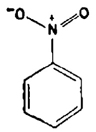

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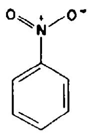

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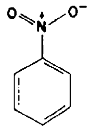

VII

indicate that calculated bond lengths for this type of molecule, derived by molecular orbital methods, are more or less worthless, but that an approximate allowance for hybridization changes gives good agreement with measured values.

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[24] T. H. Goodwin, *J. Chem. Soc.* 4451 (1955).

[25] J. Donohue and K. N. Trueblood, *Acta Cryst.* 9, 960 (1956).

It is possible of course that there are small contributions from ionic structures, which are insufficient to produce measurable shortenings of the C–N bond distances, but could affect properties such as dipole moment.

As Dewar and Schmeising[1] point out, several other properties are commonly quoted as evidence for π-delocalization in conjugated and hyperconjugated molecules. The higher dipole moment of nitrobenzene ($3{\cdot}95D$ in benzene solution) for example, in comparison with aliphatic nitro compounds ($3{\cdot}3D$), is considered as the effect of polar structures such as II and III, while the reduced moment of nitromesitylene ($3{\cdot}67D$), in comparison with nitrobenzene, is taken as evidence for steric inhibition of resonance due to deviations from coplanarity—deviations which our recent X-ray work has indicated are real. These figures suggest however that at most 40 per cent of the dipole moment differences is the result of other valence structures, the remainder being presumably due to differences in hybridization or inductive effects, probably both. The X-ray analysis of nitromesitylene indicates that the moments of the methyl groups probably do not cancel (as is assumed in the above discussion of resonance effects) since the bond angles at the methyl groups differ significantly from 120°, and also that the valency angles around the nitro group differ from the values in nitrobenzene. All these variations would have to be taken into account before the small difference of $0{\cdot}28D$ could be considered as the effect of resonance involving ionic structures.

Further consideration of this type of physical property is obviously desirable.