

## Molecular Geometry of Substituted Benzene Derivatives. III.\* On the Structural Effects of Conjugation

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(Received 5 January 1979; accepted 12 February 1979)

### Abstract

Some recent, accurate structural results obtained by different techniques for monosubstituted benzene derivatives are analysed and compared. It is shown that X-ray crystallography, whilst generally not suited for the accurate measurement of bond distances, can provide accurate values for bond angles. Evidence is given for the existence of angular distortions of the benzene nucleus caused by substitution not only in the part of the ring nearest to the substituent, but also in the opposite part. The internal angle *para* to the substituent,  $\delta$ , shows definite, albeit small, variations from  $120^\circ$ . The observed range of values is *ca*  $3^\circ$ , compared with a range of  $11^\circ$  observed for the internal angle *ipso* to the substituent,  $\alpha$ . Whilst  $\alpha$  is predominantly controlled by the  $\sigma$ -electron-withdrawing or -releasing properties of the substituent,  $\delta$  is sensitive to the perturbations occurring in the  $\pi$ -electron system of the ring; its values reflect, at least to some extent, the amount of partial charge residing on the *para* C atom.

### Introduction

Substitution of a H atom with a functional group is known to distort the C atom skeleton of the benzene ring from perfect  $D_{6h}$  ( $6/mmm$ ) symmetry (Domenicano, Vaciago & Coulson, 1975*a,b*; Domenicano, Mazzeo & Vaciago, 1976). The distortions concern mainly the half of the ring nearest the substituent, *i.e.* the *a* bonds and the  $\alpha$  and  $\beta$  angles (Fig. 1). No conclusive evidence of deformations, involving the half of the ring opposite to the substituent, was available in early 1974; it was clear, however, that any such deformation could only be small.

Since that time a detailed account of the molecular structure of aniline, determined by microwave spectroscopy,

\* Part II: Domenicano, Vaciago & Coulson (1975*b*). Part IV: Colapietro & Domenicano (1978). Part V: Colapietro, Domenicano & Pela Ceccarini (1979).

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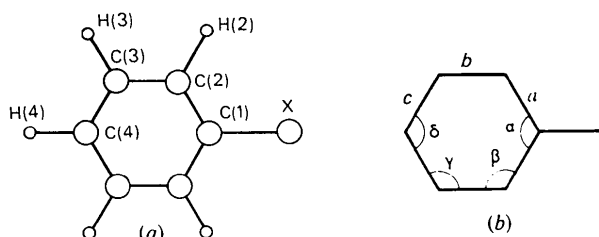


Fig. 1. Lettering of (a) the C and H atoms and (b) the C–C bonds and C–C–C angles in monosubstituted benzene derivatives.  $C_{2v}$  ( $mm$ ) symmetry has been assumed. A prime is used in the text to denote atoms, bonds or angles related to those shown here by the C(1)–C(4) diad.

copy, has been published (Lister, Tyler, Høg & Wessel Larsen, 1974). The structures of several compounds containing phenyl groups bonded to N have been accurately determined by low-temperature X-ray crystallography (Hoekstra & Vos, 1975*a,b*; Ottersen, Christophersen & Treppendahl, 1975; Tucker, Hoekstra, ten Cate & Vos, 1975). These and other results, when taken together, provide evidence of the existence of a small, systematic effect of certain substituents on  $\gamma$  and  $\delta$ . Both the experimental evidence and an interpretation of the effect are presented in this paper.

A preliminary communication of this work has been given (Domenicano & Vaciago, 1976).

### Experimental evidence

The 'substitution' structure of aniline, as obtained from the microwave spectra of 13 isotopic modifications of the molecule (Lister, Tyler, Høg & Wessel Larsen, 1974), is shown in Fig. 2(a). The C–C distances are only marginally different from the  $r_g$  value of  $1.399 \pm 0.001$  Å obtained for benzene by gas-phase electron diffraction (Tamagawa, Iijima & Kimura, 1976). However,  $\alpha$ ,  $\gamma$  and  $\delta$  show significant deviations from  $120^\circ$ .

We were puzzled by this pattern of angular distortions, different from that expected on the basis of the many examples presented in Part I of this series (Domenicano, Vaciago & Coulson, 1975*a*), and we  
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have therefore searched for further experimental support. Low-temperature X-ray diffraction results on aniline itself are not, to our knowledge, available. We have then tentatively analysed the results of the many X-ray diffraction studies that have been carried out on compounds containing the molecular fragment  $C_6H_5-NH-X$  ( $X = C, N$ ). We are aware that this procedure is open to criticism, even if it is assumed that replacing an aminic proton with a substituent has no effect on the ring geometry of aniline. The atomic coordinates obtained by microwave spectroscopy refer to the nuclei, whilst those obtained by X-ray diffraction refer to the centroids of electron density. Thus the bond angles obtained by the two techniques may show systematic differences. (It is unlikely, however, that such differences are critical in the part of the ring

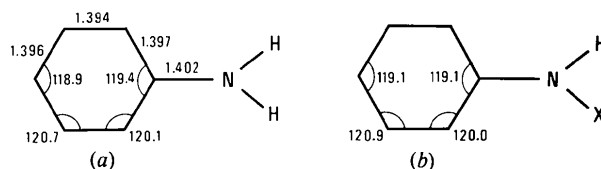


Fig. 2. (a) 'Substitution' structure ( $\text{\AA}$ ,  $^\circ$ ) of the heavy-atom skeleton of aniline, as obtained by microwave spectroscopy for the isolated molecule (Lister, Tyler, Høg & Wessel Larsen, 1974). The symmetry assumed is  $C_{2v}(mm)$ . The error limits are  $0.002\text{--}0.004$   $\text{\AA}$  for bond lengths and  $0.1\text{--}0.2^\circ$  for angles. The angle between the plane of the ring and that of the substituent is  $37.5 \pm 2.0^\circ$ . (b) Internal angles ( $^\circ$ ) of the ring in the molecular fragment  $C_6H_5-NH-X$  ( $X = C, N$ ), as obtained by X-ray crystallography. The values given are mean values from 13 benzene rings (Table 1);  $C_{2v}(mm)$  symmetry has been assumed in averaging. The s.d.'s of the means are  $0.1\text{--}0.2^\circ$ . The angle between the least-squares plane of the ring and the  $C(1)\text{--}N\text{--}X$  plane varies between  $5.3$  and  $70.3^\circ$ , with a mean of  $24.3^\circ$ .

Table 1. Internal angles ( $^\circ$ ) of the benzene ring in compounds containing the molecular fragment  $C_6H_5-NH-X$  ( $X = C, N$ ), as obtained by X-ray crystallography

No relevant compound with  $\sigma(C-C-C) \leq 0.3^\circ$  has been deliberately omitted from this table.

Number	Compound	Reference	$\alpha$	$\beta$	$\gamma$	$\delta$	$\sigma(C-C-C)$	$\tau^{a,b}$
1	Acetanilide	<i>c</i>	119.6	119.1 120.2	121.7 120.4	119.0	0.2	19.6
2	3-( <i>N</i> -Phenyl)aminopyrrolidine-2,5-dione	<i>d</i>	118.0	120.5 120.5	121.1 121.3	118.6	0.2	17.5
3	1-Phenylthiosemicarbazide	<i>e</i>	119.2	119.7 120.0	121.0 120.8	119.2	0.2	11.6
4	5-Anilino-3-oxo-2-phenyl-2,3-dihydro-1 <i>H</i> -pyrazolo[3,4- <i>d</i> ]-thiazole	<i>f</i>	119.6	119.3 120.1	121.3 120.7	119.0	0.2	25.2
5	<i>N</i> -Phenyl-2,6-dichlorobenzamide oxime	<i>g</i>	119.3	120.0 120.2	120.4 120.4	119.6	0.2–0.3	54.1
6	1,1',3,3'-Tetraphenylloxal-diamidrazone	<i>h</i>	119.1	119.9 120.1	120.8 120.7	119.3	0.1–0.2	5.3
			119.8	119.6 119.9	120.8 120.7	119.3	0.1–0.2	18.3
7	Ammonium 8-anilino-1-naphthalenesulphonate hemihydrate	<i>i, b</i>	118.8	119.6 120.1	121.2 121.6	118.5	0.3 <sup><i>j</i></sup>	10.3
			119.4	119.7 120.1	120.3 121.1	119.4	0.3 <sup><i>j</i></sup>	70.3
8	2-Phenyl-4,5-dianilino-2 <i>H</i> -1,2,3-triazole	<i>k</i>	118.3	121.0 120.4	120.5 120.7	119.2	0.3	6.1
			119.1	119.7 120.5	121.1 120.2	119.3	0.3	21.4
9	3-Pyridylcarboxanilide	<i>l</i>	120.0	119.5 119.8	121.0 120.6	119.2	0.2	31.3
10	(2-Phenylamino- <i>cis,trans</i> -3,5-heptadiene)iron tricarbonyl	<i>m, b</i>	117.8	121.4 120.1	120.5 121.1	119.1	0.2 <sup><i>j</i></sup>	25.2
	Minimum value		117.8	119.1	120.2	118.5		5.3
	Maximum value		120.0	121.4	121.7	119.6		70.3
	Mean		119.1	120.0	120.9	119.1		24.3
	Standard deviation		0.2	0.1	0.1	0.1		—

(a) Angle between the least-squares plane of the ring and the  $C(1)\text{--}N\text{--}X$  plane. (b) Calculated from the atomic and unit-cell parameters given in the original paper. (c) Brown (1966). (d) Argay & Carstensen-Oeser (1973). (e) Czugler, Kálmán & Argay (1973). (f) Smith (1969). (g) Dondoni, Gilli & Sacerdoti (1976). (h) Harlow & Simonsen (1975). (i) Cody & Hazel (1977). The asymmetric unit contains two crystallographically independent molecules. (j) Calculated from the e.s.d.'s of the atomic parameters given in the original paper. (k) Harlow, Brown, Dewar & Simonsen (1977). (l) Gdaniec & Kosturkiewicz (1978), and personal communication by the authors. (m) Immirzi (1974).

opposite to the substituent.) The measurement of the ring geometry by X-ray diffraction may also be disturbed by the effects of solid-state thermal motions. Fortunately several types of molecular motions have less pronounced effects on bond angles than on bond distances. Angles may therefore be looked at with more confidence, even if determined at room temperature (Wheatley, 1959).

Table 1 shows the values of the internal angles of the benzene ring in a number of compounds containing the molecular fragment  $C_6H_5-NH-X$  ( $X = C, N$ ). All values have been obtained by X-ray diffraction.\* Table 1 reveals for each molecule a pattern of angular distortions similar to that observed in aniline. Averaging over all entries yields the mean values of  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  shown in Fig. 2(b). The agreement with the microwave results of Fig. 2(a) is surprisingly good, in spite of the previous cautionary considerations. This leaves little doubt about the significance of the distortions from  $120^\circ$  of  $\gamma$  and  $\delta$ , and also shows that X-ray diffraction, whilst generally not suited for the accurate measurement of bond distances, can provide accurate values for bond angles.

Strikingly similar effects occur in the pyridine nucleus when any of the three chemically non-equivalent H atoms is replaced by an amino group. This is apparent from Fig. 3, where the internal angles of the ring in 2-aminopyridine (Chao, Schempp & Rosenstein, 1975a), 3-aminopyridine (Chao, Schempp & Rosenstein, 1975b) and 4-aminopyridine (Chao & Schempp, 1977) are compared with those of unsubstituted pyridine (Sørensen, Mahler & Rastrup-Andersen, 1974). The presence of the amino group not only affects  $\alpha$ ,  $\beta$  and  $\gamma$ , as discussed in detail by Chao & Schempp (1977), but also acts on the opposite part of the ring, giving rise to a small decrease of  $\delta$  and a small increase of  $\gamma$ .

\* C—C lengths are not reported; they are almost invariably shorter than the corresponding spectroscopic value for aniline.

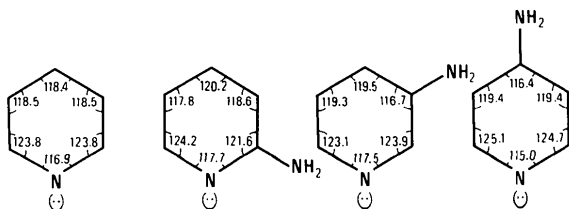
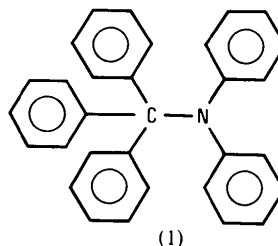


Fig. 3. Comparison of the internal angles ( $^\circ$ ) of the ring in pyridine and monoaminopyridines. The angles for pyridine refer to the 'substitution' structure obtained by microwave spectroscopy for an isolated molecule of  $C_{2v}$  ( $mm$ ) symmetry (Sørensen, Mahler & Rastrup-Andersen, 1974). Although the e.s.d.'s,  $\sigma$ , given in the original paper are *ca*  $0.01^\circ$ , we quote here only one decimal figure, the second being irrelevant to the present comparison. The angles for the aminopyridines have been obtained by room-temperature X-ray crystallography (Chao, Schempp & Rosenstein, 1975a,b; Chao & Schempp, 1977). The  $\sigma$  values are *ca*  $0.2^\circ$  for 2- and 4-aminopyridine,  $0.3^\circ$  for 3-aminopyridine.

The distortions of  $\gamma$  and  $\delta$  occurring in aniline and in the aminopyridines appear to be related to the interaction of the N lone pair with the  $\pi$ -electron system of the ring. Experimental evidence on this point is given by the structural results presented below.



A low-temperature (113 K) X-ray diffraction study of diphenylaminotriphenylmethane (1) shows that the N atom is in a perfectly planar configuration (Hoekstra & Vos, 1975a,b). The two phenyl groups bonded to N have different conformations: the angles between the coordination plane of N and the least-squares planes of the rings are  $12.4^\circ$  and  $74.6^\circ$ , respectively. Both angles are mainly torsions about N—C(1). The different conformations strongly affect the extent of conjugation of the rings with the substituent, as witnessed by the different lengths of the two N—C(1) bonds [ $1.405$  (1) *vs*  $1.438$  (1) Å]. The detailed geometries of the two benzene rings are compared in Fig. 4. The differences in the values of several structural parameters ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and  $a$ ) are highly significant, and may only be caused by the different extent of the interaction between the N lone pair and the  $\pi$ -electron system of the ring. It should be noted that  $\gamma$ ,  $\gamma'$  and  $\delta$  are almost  $120^\circ$  when the conformation of the ring is unfavourable to conjugation.

Additional evidence is obtained by comparing the molecular structures of *N*-[3-phenyl-5-(1,2,3,4-oxatriazolio)]phenylamide (2) and *N*-(diphenylmethylene)aniline (3). Both molecules have been studied by low-temperature (113/103 K) X-ray

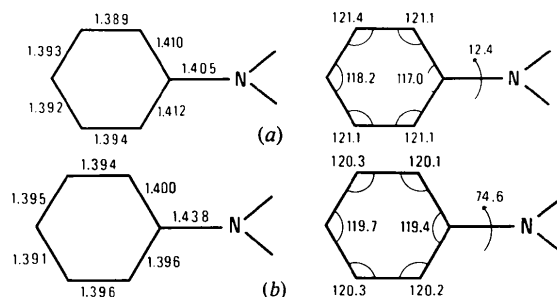
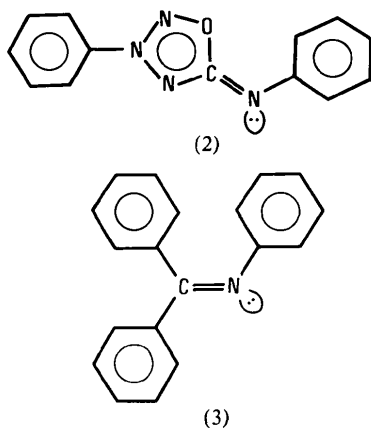


Fig. 4. Comparison of the ring geometries ( $\text{\AA}$ ,  $^\circ$ ) of the two phenyl groups bonded to N in diphenylaminotriphenylmethane (1), as determined by low-temperature X-ray crystallography (Hoekstra & Vos, 1975a,b). E.s.d.'s are *ca*  $0.001$  Å and  $0.1^\circ$ . The angle between the coordination plane of N and the least-squares plane of the ring is (a)  $12.4^\circ$  for one phenyl group and (b)  $74.6^\circ$  for the other.



crystallography (Ottersen, Christophersen & Treppendahl, 1975; Tucker, Hoekstra, ten Cate & Vos, 1975). They contain an identical fragment,  $C_6H_5-N=C<$ , again in different conformations. The angle between the least-squares plane of the ring and the  $C(1)-N=C$  plane is  $6.2^\circ$  in (2) and  $63.4^\circ$  in (3), both angles being mainly torsions about  $N-C(1)$ . The effect of the different conformations on the geometry of the ring (Fig. 5) is similar to that of the previous example.

### Discussion

On the basis of the evidence presented in the preceding section the effect of  $\pi$ -electron-releasing substituents on the geometry of the benzene ring may be described as resulting from two separate, superposed effects.

The first effect is a decrease of  $\alpha$ , accompanied by a lengthening of  $a$  and  $a'$  and by an increase of  $\beta$  and  $\beta'$ .

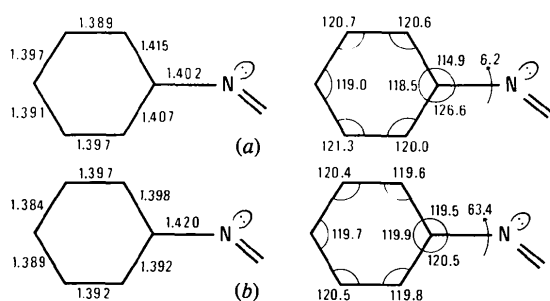


Fig. 5. Comparison of the ring geometries ( $\text{\AA}$ ,  $^\circ$ ) of the molecular fragment  $C_6H_5-N=C<$  in (a) *N*-[3-phenyl-5-(1,2,3,4-oxatriazolol)]phenylamide (2) (Ottersen, Christophersen & Treppendahl, 1975) and (b) *N*-(diphenylmethylene)aniline (3) [(Tucker, Hoekstra, ten Cate & Vos, 1975); the geometry shown here has been calculated from the atomic and unit-cell parameters given in the original paper]. Both structures have been determined by low-temperature X-ray crystallography. E.s.d.'s are  $0.003 \text{ \AA}$  and  $0.2^\circ$  for (2),  $0.002 \text{ \AA}$  and  $0.15^\circ$  for (3). The minor deviations from axial symmetry in the ring geometry of (2) may be caused by the large bending of the substituent in the plane of the ring, as in *para*-substituted anisoles (Di Rienzo, Domenicano, Portalone & Vaciago, 1976).

It has already been described in detail and attributed to the shortening of  $C(1)-X$  (Domenicano, Vaciago & Coulson, 1975a).

The second effect is a decrease of  $\delta$ , and also, to some extent, of  $\beta$  and  $\beta'$ , accompanied by an increase of  $\gamma$  and  $\gamma'$ . It is tempting to relate this effect to the well-known pattern of partial negative charges induced by  $\pi$ -donor functional groups on  $C(4)$ ,  $C(2)$  and  $C(2')$ . Indeed the decrease of  $\delta$ ,  $\beta$ , and  $\beta'$  may be explained qualitatively by considering that a C atom bearing a partial negative charge has a slightly greater covalent radius than a neutral C, hence is pushed away from the centre of the ring. It should be noted that the two effects have opposing actions on  $\beta$  and  $\beta'$ , whereupon they partly cancel each other.

The distortions of the ring geometry caused by conjugation are in turn superposed on those arising from the  $\sigma$ -electron-withdrawing or -releasing properties of the substituent (Domenicano, Vaciago & Coulson, 1975a).

It is well known that certain substituents, *e.g.* methyl and *tert*-butyl groups, although lacking unshared electron pairs, are able to cause a perturbation of the  $\pi$ -electron system of the ring very much like that caused by  $\pi$  donors. This is traditionally attributed to hyperconjugation, but various MO calculations carried out on toluene support the idea that the  $\pi$ -electron system of the ring is polarized by the methyl group, with little net electron transfer (Libit & Hoffmann, 1974). We expect angular distortions to occur in the benzene ring of these molecules, similar to those caused by  $\pi$ -donor functional groups. Structural data for toluene are available by three different techniques, namely low-temperature X-ray crystallography (Kirner, Reed & Scheidt, 1977), gas-phase electron diffraction (Domenicano, Schultz, Kolonits & Hargittai, 1979), and MO calculations with full optimization of molecular geometry (Gleghorn, 1977; Gleghorn & McConkey, 1976). These data are compared in Table 2: they all show the expected trend in the ring bond

Table 2. Comparison of the ring bond angles ( $^\circ$ ) in toluene, as obtained by different techniques

Technique	Reference	$\alpha$	$\beta$	$\gamma$	$\delta$
Low-temperature X-ray crystallography	<i>a</i>	117.5 (3)	121.1 (4) 121.3 (4)	120.6 (3) 120.5 (4)	119.0 (3)
Gas-phase electron diffraction	<i>b</i>	$118.7 \pm 0.4$	$120.4 \pm 0.4$	$120.6 \pm 0.5$	$119.4 \pm 0.6$
MO calculations	<i>c</i>	117.5	121.4	120.2	119.3

(a) From the results of a crystal structure analysis of the toluene solvate of  $\alpha,\beta,\gamma,\delta$ -tetraphenylporphatomanganese(II), carried out at 98 K (Kirner, Reed & Scheidt, 1977). The angles given here have been calculated from the atomic and unit-cell parameters given in the original paper. E.s.d.'s are given in parentheses as units in the last digit.

(b) Domenicano, Schultz, Kolonits & Hargittai (1979). This refinement of the molecular structure of toluene is based on the electron diffraction intensities of Seip, Schultz, Hargittai & Szabó (1977); the ring has been constrained to  $C_{2v}$  (*mm*) symmetry. Uncertainties are given as maximum errors.

(c) Gleghorn (1977); slightly different values were given by Gleghorn & McConkey (1976). The molecular geometry has been optimized to minimum energy by SCF-MO calculations in the MINDO/2' approximation.

angles. The detailed molecular geometry of *tert*-butylbenzene is unknown, but a sound estimate of the ring bond angles in this molecule may be obtained by averaging the results of the many X-ray diffraction analyses that have been carried out on compounds

containing the molecular fragment  $C_6H_5-C \begin{matrix} \diagup C \\ \diagdown C \end{matrix}$ . These

results are shown in Table 3. They yield a pattern of angular distortions of the benzene ring very close to that observed in toluene.

The presence of a partial positive charge on C(4), as caused by *e.g.*  $\pi$ -acceptor functional groups, should

give rise to opposite distortions of  $\gamma$  and  $\delta$ . Accurate experimental results providing direct evidence for this effect are not yet available.\* MO calculations with full

\* Reasonably sound evidence may be derived from experimental results of moderate accuracy. A mean value of  $120.5(1)^\circ$  is obtained for  $\delta$  from the structures of the phenylphosphonium cations listed in Table 3 of Part II of this series (Domenicano, Vaciego & Coulson, 1975*b*). The 16 individual values of  $\delta$  are not very accurate, nor are they particularly precise [ $\sigma(\delta) = 0.2-0.6^\circ$ ]; the range, however, is rather narrow,  $120.0-121.1^\circ$ , and we are inclined to think that the effect is real. The mean value of  $\gamma$  is  $120.2(1)^\circ$ . Similar distortions of the benzene ring are also observed in phenylsulphones.

Table 3. Internal angles ( $^\circ$ ) of the benzene ring in compounds containing the molecular fragment  $C_6H_5-C \begin{matrix} \diagup C \\ \diagdown C \end{matrix}$ , as obtained by X-ray crystallography

The following have not been considered for inclusion in this table: (i) compounds having a phenyl group bonded to a three- or four-membered ring; (ii) compounds with strongly  $\sigma$ -electron-withdrawing moieties bonded to the exocyclic C atom; (iii) structure analyses in which the H-atom contribution was not included in the scattering model used in the refinement; (iv) structure analyses giving  $\sigma(C-C-C) > 0.3^\circ$ .

Number	Compound	Reference	$\alpha$	$\beta$	$\gamma$	$\delta$	$\sigma(C-C-C)$
1	Tetraphenylmethane	<i>a, b</i>	117.5	121.3 121.2	120.3 120.4	119.3	0.2 <sup>c</sup>
			117.6	121.2 120.6	120.6 121.0	119.0	0.3 <sup>c</sup>
			117.5	121.3 121.2	120.1 120.1	119.9	0.2 <sup>c</sup>
2	$\alpha$ -2-Ethyl-5-methyl-3,3-diphenyl-tetrahydrofuran	<i>d</i>	117.9	120.7 121.1	120.8 120.3	119.2	0.3
			117.2	120.9 121.5	120.7 120.3	119.3	0.3
3	6-Dimethylamino-4,4-diphenyl-3-heptanone (methadone)	<i>e</i>	116.6	121.7 121.4	120.6 120.7	119.0	0.2-0.3
			117.6	120.9 121.1	121.0 120.2	119.1	0.2-0.3
4	6-Dimethylamino-4,4-diphenyl-3-heptanone (methadone)	<i>f, b</i>	117.4	121.5 121.0	120.7 121.0	118.3	0.3 <sup>c</sup>
			117.9	120.5 120.6	120.8 121.4	118.8	0.3 <sup>c</sup>
5	2,2-Diphenyl-3-methyl-4-( <i>N</i> -morpholino)butanoic acid <i>N</i> -pyrrolidinylamide (dextromoramide)	<i>g</i>	116.6	121.2 121.9	121.2 120.1	118.9	0.3
			116.5	121.9 122.0	120.0 119.6	119.8	0.3
6	1-Benzyl-4-(2,6-dioxo-3-phenyl-3-piperidyl)piperidine	<i>h</i>	117.8	120.6 120.8	120.8 120.8	119.1	0.3
7	2-Diethylaminoethyl 1-phenylcyclopentanecarboxylate hydrochloride (parpanit)	<i>i</i>	117.4	121.0 121.2	120.3 120.0	120.0	0.2-0.3 <sup>c</sup>
8	1-Phenyl-4- <i>tert</i> -butylcyclohexane-1-carboxylic acid	<i>j</i>	118.1	120.9 120.2	120.7 121.3	118.9	0.3
9	( <i>E</i> )-2-Chlorovinylidene-5-phenyladamantane	<i>k, b</i>	116.8	121.3 121.8	120.7 120.1	119.3	0.2
	Minimum value		116.5	120.2	119.6	118.3	
	Maximum value		118.1	122.0	121.4	120.0	
	Mean		117.4	121.1	120.6	119.2	
	Standard deviation		0.1	0.1	0.1	0.1	

(*a*) Robbins, Jeffrey, Chesick, Donohue, Cotton, Frenz & Murillo (1975); the paper describes the results of three independent analyses. The molecule has  $S_4(4)$  crystallographic symmetry. (*b*) The bond angles have been calculated from the atomic and unit-cell parameters given in the original paper. (*c*) Calculated from the e.s.d.'s of the atomic parameters given in the original paper. (*d*) Singh & Ahmed (1969). (*e*) Bye (1974). (*f*) Bürgi, Dunitz & Shefter (1973). (*g*) Bye (1976). (*h*) Koch & Dideberg (1973). (*i*) Griffith & Robertson (1972). (*j*) Chiaroni, Riche & Pascard-Billy (1974). (*k*) Okaya, Maluszynska, Chiou & le Noble (1978).

Table 4. Calculated internal angles ( $^{\circ}$ ) of the benzene ring in derivatives with very strong  $\pi$ -acceptor substituents

All values have been obtained by SCF-MO calculations with full optimization of molecular geometry.

Number	Compound	Reference	Technique	$\alpha$	$\beta$	$\gamma$	$\delta$
1	Benzoyl cation	<i>a</i>	INDO	120.0	119.9	119.5	121.2
2	3-Phenylpropynoyl cation	<i>a</i>	INDO	119.8	120.1	119.4	121.3
3	Benzenediazonium cation	<i>b</i>	<i>ab initio</i> (STO-3G basis set)	125.2	116.5	120.2	121.6

(*a*) Pittman, Kim, Ng & Kispert (1976). (*b*) Vincent & Radom (1978).

optimization of molecular geometry have, however, been carried out on at least three systems with very strong  $\pi$ -acceptor substituents, namely the benzoyl, 3-phenylpropynoyl, and benzenediazonium cations (Pittman, Kim, Ng & Kispert, 1976; Vincent & Radom, 1978). The calculated ring angles for these systems are reported in Table 4: they are in excellent agreement with our prediction.

### Conclusions

The structural results analysed in this paper show that in monosubstituted benzene derivatives the internal angle *para* to the substituent,  $\delta$ , is sensitive to the perturbations caused by the substituent in the  $\pi$ -electron system of the ring, and reflects, at least to some extent, the amount of partial charge residing on C(4).<sup>\*</sup> The range of the values reported for  $\delta$  is *ca*  $3^{\circ}$ . This is considerably less than the  $11^{\circ}$  range observed for  $\alpha$ , a parameter that is predominantly controlled by the  $\sigma$ -electron-withdrawing or -releasing properties of the substituent (Domenicano, Mazzeo & Vaciago, 1976).

In Part I of this series (Domenicano, Vaciago & Coulson, 1975*a*) the rule was proposed that the value of  $\alpha$  associated with a given functional group was essentially unaffected by the presence of a *para* substituent. Exceptions were shown to occur with benzene derivatives having a strong  $\pi$  donor *para* to a  $\pi$  acceptor and were attributed to through-conjugation. The results presented here explain the approximate character of the rule, and suggest that deviations may be observed with any *para* substituent able to distort  $\delta$  appreciably from  $120^{\circ}$ . Experimental work is in progress in our laboratories on a number of *para*-substituted derivatives of benzoic acid (Colapietro & Domenicano, 1977, 1978; Colapietro, Domenicano & Pela Ceccarini, 1979; Colapietro, Domenicano & Marcianite, 1978), with the aim of measuring the effect of different substituents on the ring geometry, and particularly on the value of the endocyclic angle at the carboxy group,  $\alpha_{\text{COOH}}$ .

<sup>\*</sup> This does not necessarily imply that the origin of the  $\delta$  scale is exactly at  $120.0^{\circ}$ .

We thank Mrs C. Marcianite for the preparation of the drawings.

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## C—H...O Interactions and Stacking of Water Molecules between Pyrimidine Bases in 5-Nitro-1-( $\beta$ -D-ribosyluronic acid)—Uracil Monohydrate [1-(5-Nitro-2,4-dioxypyrimidinyl)- $\beta$ -D-ribofuranic Acid Monohydrate]: A Neutron Diffraction Study at 80 K\*

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(Received 9 August 1978; accepted 29 January 1979)

### Abstract

A low-temperature neutron diffraction study of the title compound has been carried out [ $C_9H_9N_3O_9 \cdot H_2O$ ,  $P2_1$ ,  $Z = 2$ ,  $a = 8.935$  (1),  $b = 10.223$  (2),  $c = 6.530$  (1) Å,  $\beta = 93.32$  (1)°, at  $T = 80$  K]. The unweighted  $R$  value based on  $F^2$  for 1602 reflections is 0.049. The present neutron diffraction analysis has resulted in the definitive characterization of the hydrogen-bonding scheme in this material. All C—H, N—H and O—H covalent bond

distances have been determined with precision better than 0.006 Å. The water molecules stack between pyrimidine bases, and the entire structure consists of layers nearly perpendicular to the  $c$  axis. The water molecules are each connected by means of O—H...O hydrogen bonds to three nucleoside molecules from neighboring stacks in approximately trigonal fashion, thus producing a 'slip-sandwich' type of arrangement. There is no direct hydrogen bonding along individual stacks. The presence of an unusually short intramolecular C—H...O hydrogen bond involving the proton on C(6) of uracil has been confirmed [ $H(C6) \cdots O(5')$  2.080 (6) Å;  $C(6) - H(C6) \cdots O(5')$  155.7 (4)°]. This interaction, which stabilizes the *anti* conformation of the nucleoside, may be enhanced by polarization of

\* Research carried out at Brookhaven National Laboratory under contract with the US Department of Energy, and supported by its Office of Basic Energy Sciences.

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