

esters (Broadhurst, 1962). In fact, many molecules may suffer analogous changes in their crystal packing arrangements as an appended alkyl group is lengthened or shortened. It should be possible to catalog and exploit these changes in designing materials for specific uses (e.g. Nicoud & Twieg, 1987).

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Electrostatic Potentials from Charge-Density Studies of Benzamide at 123 K

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Abstract

C_7H_7NO , $M_r = 121.14$, monoclinic, $P2_1/c$, $a = 5.549$ (1), $b = 5.033$ (1), $c = 21.548$ (4) Å, $\beta = 89.22$ (1)°, $V = 601.74$ (1) Å³, $D_x = 1.35$ Mg m⁻³, $\lambda(\text{MoK}\alpha) = 0.71069$ Å, $\mu = 0.086$ mm⁻¹, $F(000) = 256$, $T = 123$ K, final $R = 0.049$, $wR = 0.047$, $S = 1.457$ for 3527 reflections and 213 parameters, including multipole electron-population parameters up to octapole for non-H atoms and quadrapole for H atoms.

Introduction

A charge-density study of benzamide was undertaken as part of a study of the charge density of benzene and its derivatives obtained by experimental methods and theoretical calculations (Jeffrey, Ruble, McMullan & Pople, 1987; Stewart, 1991). Electrophilic aromatic

substitution has been examined by a number of different researchers. March (1992), Carey & Sundberg (1990) and Taylor (1990) agree that first the rapid formation of a π -complex occurs, followed by the slower formation of a σ -complex in which one C atom has a H plus the electrophile, followed finally by the rapid loss of either the H or the electrophile. The orientational effects observed in monosubstituted aromatic compounds are caused by stabilization of one σ -complex and destabilization of the other. Pauling (1960) points out that the distribution of charge in the molecule undergoing substitution is an important consideration in determining the orientation of the next substituent. Since the substituent in benzamide is a *meta*-director for further electrophilic addition, there was a question as to whether this effect would be observed in the electrostatic potential, or whether it would be masked by intermolecular interactions. Results of the present study are

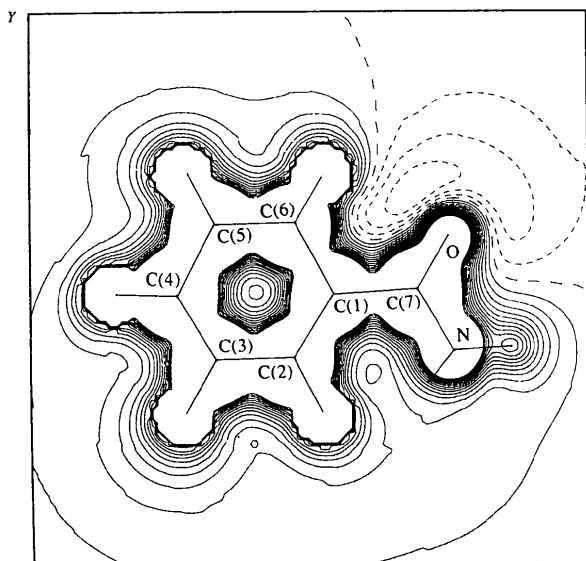


Fig. 1. The electrostatic potential in the plane of the benzene ring. Contours are $0.05 \text{ e } \text{\AA}^{-1}$.

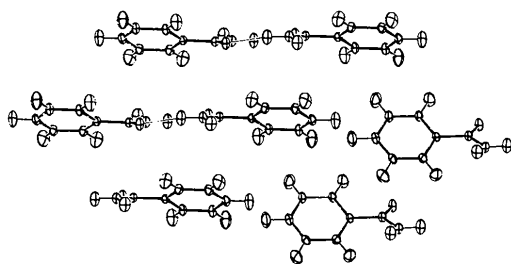


Fig. 2. Packing diagram for benzamide with 50% probability ellipsoids.

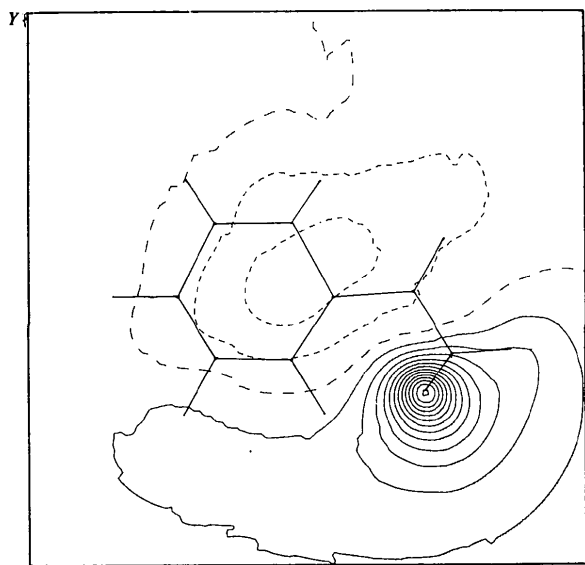


Fig. 3. The electrostatic potential 1.6 \AA above the plane of the benzene ring. Contours are $0.05 \text{ e } \text{\AA}^{-1}$.

presented as maps of the electrostatic potential (Figs. 1 and 3–5) derived from the experimental charge-density distribution (Stewart & Craven, 1993).

Experimental

Crystals of benzamide were grown from benzene solution by slow evaporation. A crystal of dimensions $0.50 \times 0.50 \times 0.38$ mounted on a glass fiber on a CAD-4 diffractometer was cooled until the c -cell dimension matched that of the corresponding neutron diffraction

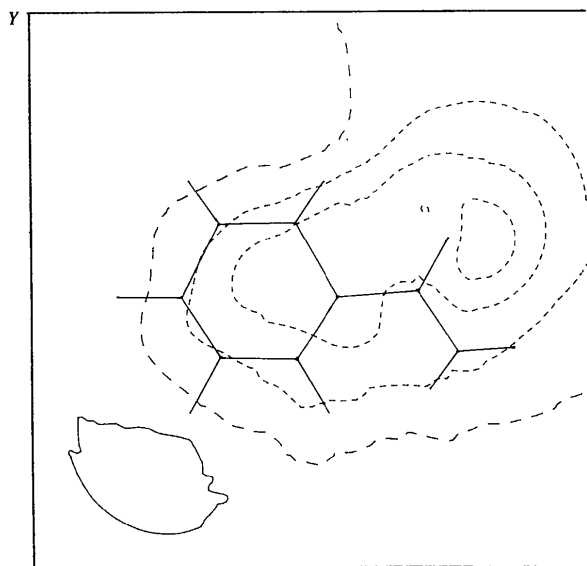


Fig. 4. The electrostatic potential 1.6 \AA below the plane of the benzene ring. Contours are $0.05 \text{ e } \text{\AA}^{-1}$.

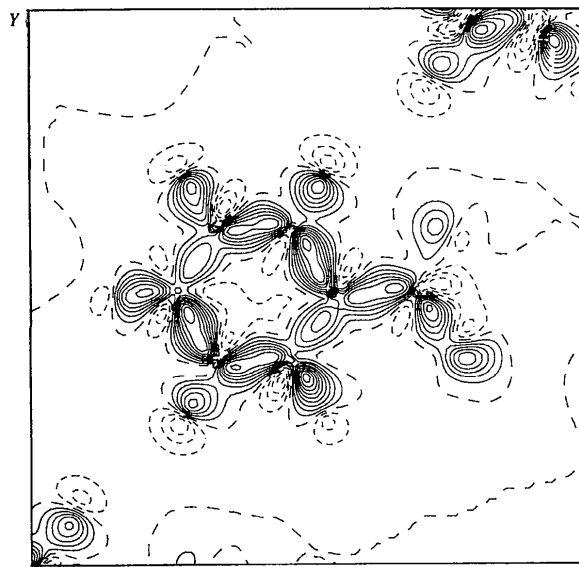


Fig. 5. The deformation density in the plane of the benzene ring. Contours are $0.1 \text{ e } \text{\AA}^{-1}$.

Table 1. Atomic positional and thermal parameters from neutron refinement

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
C(1)	0.47492 (15)	0.06764 (17)	0.10953 (4)	0.0150 (4)	0.0115 (3)	0.0167 (2)	-0.0006 (3)	-0.0028 (3)	-0.0013 (3)
C(2)	0.64748 (17)	0.26935 (19)	0.10486 (4)	0.0194 (4)	0.0175 (4)	0.0195 (5)	-0.0053 (3)	-0.0029 (3)	0.0002 (3)
C(3)	0.82423 (17)	0.29445 (20)	0.14980 (5)	0.0176 (4)	0.0209 (4)	0.0234 (5)	-0.0053 (3)	-0.0037 (3)	-0.0029 (3)
C(4)	0.82792 (17)	0.11971 (21)	0.19992 (5)	0.0170 (4)	0.0223 (4)	0.0243 (3)	-0.0005 (3)	-0.0069 (3)	-0.0033 (3)
C(5)	0.65380 (18)	-0.07923 (20)	0.20525 (4)	0.0209 (4)	0.0200 (4)	0.0227 (5)	-0.0004 (3)	-0.0085 (4)	0.0025 (3)
C(6)	0.47921 (17)	-0.10644 (18)	0.16000 (4)	0.0183 (4)	0.0145 (4)	0.0208 (5)	-0.0019 (3)	-0.0061 (3)	0.0027 (3)
C(7)	0.28637 (16)	0.02791 (16)	0.06140 (4)	0.0169 (4)	0.0106 (3)	0.0167 (5)	-0.0002 (3)	-0.0039 (3)	-0.0009 (3)
O	0.19589 (21)	-0.19510 (20)	0.05334 (5)	0.0237 (5)	0.0103 (4)	0.0261 (5)	-0.0015 (4)	-0.0107 (4)	-0.0011 (3)
N	0.22277 (12)	0.23983 (13)	0.02795 (3)	0.0219 (3)	0.0124 (2)	0.0204 (2)	-0.0007 (2)	-0.0066 (2)	0.0009 (2)
H(2)	0.64685 (46)	0.40519 (53)	0.06556 (11)	0.0466 (13)	0.0398 (12)	0.0344 (9)	-0.0170 (10)	-0.0068 (9)	0.0144 (9)
H(3)	0.95821 (44)	0.45049 (54)	0.14538 (12)	0.0377 (12)	0.0422 (13)	0.0494 (14)	-0.0212 (10)	-0.0072 (10)	0.0010 (11)
H(4)	0.96479 (43)	0.13881 (57)	0.23501 (12)	0.0352 (11)	0.0490 (14)	0.0423 (12)	-0.0072 (10)	-0.0207 (10)	0.0002 (10)
H(5)	0.65328 (48)	-0.21417 (55)	0.24475 (12)	0.0479 (13)	0.0425 (13)	0.0416 (12)	-0.0068 (11)	-0.0179 (10)	0.0173 (10)
H(6)	0.34514 (43)	-0.26302 (48)	0.16299 (12)	0.0389 (11)	0.0302 (10)	0.0457 (12)	-0.0151 (9)	-0.0142 (9)	0.0115 (9)
H(7)	0.08546 (39)	0.21870 (43)	-0.00281 (10)	0.0355 (10)	0.0268 (9)	0.0337 (9)	-0.0007 (8)	-0.0161 (8)	0.0012 (8)
H(8)	0.26573 (41)	0.42622 (40)	0.04160 (10)	0.0376 (11)	0.0194 (8)	0.0380 (9)	-0.0037 (8)	-0.0098 (8)	0.0002 (8)

Table 2. Benzamide population parameters

	<i>p_v</i>	<i>d</i> ₁	<i>d</i> ₂	<i>d</i> ₃	<i>q</i> ₁	<i>q</i> ₂	<i>q</i> ₃	<i>q</i> ₄	<i>q</i> ₅
C(1)	4.18 (7)	0.30 (18)	0.18 (17)	0.03 (17)	-0.21 (16)	1.06 (16)	0.43 (16)	-0.69 (17)	2.68 (17)
C(2)	4.07 (7)	-0.65 (19)	0.25 (21)	-0.02 (22)	0.09 (18)	0.66 (18)	0.82 (19)	-1.34 (19)	3.23 (20)
C(3)	3.86 (7)	-0.67 (21)	-0.57 (22)	-0.11 (20)	0.22 (20)	0.87 (19)	0.75 (19)	-1.22 (19)	3.39 (20)
C(4)	4.00 (8)	-0.43 (21)	0.57 (21)	-0.78 (21)	0.30 (18)	1.14 (20)	0.18 (19)	-0.97 (21)	2.82 (21)
C(5)	3.91 (8)	0.34 (20)	0.85 (22)	-1.11 (22)	0.55 (20)	0.99 (19)	0.67 (19)	-0.39 (20)	2.78 (21)
C(6)	3.96 (7)	0.47 (21)	0.73 (21)	-0.59 (19)	0.59 (19)	0.92 (19)	0.66 (18)	-1.09 (18)	3.03 (19)
C(7)	3.81 (7)	0.59 (19)	0.36 (18)	0.20 (18)	-1.16 (17)	1.05 (17)	1.27 (17)	-1.11 (18)	2.29 (17)
O	6.39 (7)	-0.37 (12)	-0.20 (12)	-0.10 (12)	-0.14 (13)	-0.32 (12)	0.42 (14)	-0.10 (13)	3.02 (15)
N	4.98 (10)	0.32 (17)	-0.38 (19)	-0.01 (17)	0.40 (17)	-0.44 (16)	-0.35 (18)	0.25 (17)	2.92 (18)
H(2)	0.91 (5)	-0.05 (26)	-0.66 (28)	0.76 (29)	0.70 (35)	0.15 (33)	-0.36 (36)	-0.25 (39)	0.21 (37)
H(3)	1.01 (6)	-1.75 (27)	-2.12 (29)	-0.01 (27)	-0.34 (38)	0.46 (40)	0.05 (39)	0.20 (37)	-0.44 (36)
H(4)	1.01 (5)	-0.65 (28)	-0.19 (28)	-1.57 (28)	-0.45 (36)	-0.04 (36)	1.06 (39)	-0.08 (37)	1.02 (40)
H(5)	1.03 (6)	0.15 (28)	1.15 (29)	-2.16 (30)	0.27 (36)	0.08 (37)	-0.85 (38)	-1.06 (37)	0.84 (39)
H(6)	1.06 (5)	1.73 (27)	2.48 (26)	-0.30 (27)	0.02 (35)	1.04 (38)	-0.16 (36)	-0.13 (36)	-0.37 (36)
H(7)	0.94 (5)	1.07 (28)	0.11 (24)	1.35 (27)	0.64 (33)	-0.02 (33)	0.86 (36)	0.05 (32)	0.71 (34)
H(8)	0.88 (5)	-0.48 (25)	-2.25 (29)	-0.14 (26)	-0.10 (35)	1.08 (36)	0.31 (33)	0.21 (36)	-0.03 (34)
C(1)		<i>o</i> ₁	<i>o</i> ₂	<i>o</i> ₃	<i>o</i> ₄	<i>o</i> ₅	<i>o</i> ₆	<i>o</i> ₇	
C(2)		-1.16 (21)	0.56 (21)	-1.45 (22)	-0.46 (23)	-1.14 (21)	-1.12 (22)	1.13 (23)	
C(3)		0.80 (22)	-0.82 (24)	1.79 (24)	0.46 (26)	1.56 (24)	2.08 (24)	-0.69 (26)	
C(4)		-1.08 (23)	0.69 (24)	-0.62 (25)	-0.61 (28)	-1.23 (26)	-1.00 (25)	0.37 (28)	
C(5)		1.09 (24)	-0.64 (25)	1.92 (25)	0.36 (28)	2.13 (25)	1.55 (27)	-0.66 (27)	
C(6)		-0.71 (23)	0.65 (24)	-0.89 (25)	-0.40 (27)	-0.85 (25)	-1.39 (25)	0.74 (28)	
C(7)		0.97 (22)	-0.46 (23)	1.18 (23)	0.51 (26)	1.35 (23)	1.33 (24)	0.18 (25)	
O		1.63 (22)	0.56 (22)	1.93 (22)	0.93 (23)	0.92 (21)	1.19 (23)	0.69 (23)	
N		-0.39 (16)	-0.43 (17)	-0.05 (18)	0.00 (18)	-0.17 (17)	-0.29 (17)	0.24 (18)	
		-1.22 (20)	-0.41 (21)	-1.40 (21)	-0.03 (22)	-0.84 (20)	-1.31 (22)	-0.61 (21)	

study (Gao, Jeffrey, Ruble & McMullan, 1991), thus assuring a matching temperature of 123 K for X-ray data collection. Data were collected using a maximum scan speed of 3.3° min⁻¹ and a maximum time of 2 min, collecting full quadrants to $\theta = 40^\circ$ ($-9 \leq h \leq 9$, $0 \leq k \leq 9$, $0 \leq l \leq 38$) and collecting a list of specified reflections with $F_{\text{calc}} \geq 5$, from $40 < \theta \leq 65^\circ$ ($0 \leq h \leq 12$, $0 \leq k \leq 11$, $-44 \leq l \leq 44$). Approximate Bragg intensities were calculated using the thermal and positional parameters determined in the neutron diffraction study (Gao *et al.*, 1991). Data were corrected for the 6% variation shown by three standard reflections collected every 100 min. A total of 4179 reflections were measured with 4035 being independent and 3527 considered observed ($I > 0$). Data were reduced using profile fitting (Blessing, 1986), corrected for absorption (de Meulenaer & Tompa, 1965; Templeton &

Templeton, 1973; $T_{\text{min}} = 0.96$, $T_{\text{max}} = 0.97$) and redundant reflections were removed.

The refinement was performed using the POP κ refinement program (Craven, Weber, He & Klooster, 1993), holding the positional and thermal parameters fixed at the neutron values (Table 1) and refining up to octapole terms for non-H atoms and up to quadrupole terms of H atoms, four κ values (for C, N, O and H), an overall scale factor and an isotropic extinction factor (Becker & Coppens, 1974). This gave 212 parameters with no constraint on the total number of valence-shell electrons and 3527 reflections which converged with $R = 0.049$, $wR = 0.047$, $S = 1.46$ and an isotropic extinction factor $g = 0.19 (4) \times 10^{-4} \text{ rad}^{-1}$. None of the p_v parameters were significantly different from those of an earlier constrained refinement so they were renormalized to a total of 46 valence electrons (Table

2).* The final difference density map gave $\Delta\rho = \pm 0.2 e \text{ \AA}^{-3}$.

Results and discussion

The electrostatic potential (Fig. 1) is shown for a molecule of benzamide which is removed from the crystal, but which retains the effects of its crystal environment. There is surprisingly good agreement between the electrostatic potential of the phenyl ring for this model (Fig. 1) and that of benzene itself (Stewart, 1991). There are no significant variations in potential around C(3) and C(5) which might account for the *meta*-directing properties of the molecule. The population parameters given in Table 2 show no indication of an increased density at these positions. The potential in the C(2) and C(6) region is similar, being only slightly contracted. The apparent minor differences between the electrostatic potential for benzene and that for benzamide are probably due to several factors. One is that the O—C(7)—C(1)—C(6) torsion angle of $-25.3(1)^\circ$ observed in the crystal structure precludes resonance between the phenyl ring and the substituent. Another is that hydrogen bonding minimizes the inductive effect. Other than hydrogen bonding, there are no significant intermolecular interactions less than 3.4 Å. A packing diagram is given in Fig. 2. A third factor could be that the

effects of the amido substituent are much weaker and might only be observable in the σ -complex itself. The deformation density (Fig. 5) for the non-H atoms in benzamide is similar to that observed in *para*-fluorobenzamide (Kubota & Ohba, 1992), which has an O—C(7)—C(1)—C(2) torsion angle of $-26.7(3)^\circ$.

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* A list of observed and calculated structure factors and electrostatic potential diagrams have been deposited with the IUCr (Reference: BK0008). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 1,3,5-Trichloro-2,4,6-trimethylbenzene at 150 and 297 K, Molecular Motion and Reorientation

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Abstract

$\text{C}_9\text{H}_3\text{Cl}_3$, triclinic $P\bar{1}$ with $Z=2$, $M_r=223.53$, crystal data at 150 K [297]: $a=7.646(3)$ [7.738(6)], $b=8.789(6)$ [8.842(4)], $c=8.827(3)$ Å [8.880(3)], $\alpha=59.78(4)$ [59.74(3)], $\beta=66.03(3)$ [66.51(5)], $\gamma=72.69(4)^\circ$ [73.06(4)], $V=465.1 \text{ \AA}^3$ [478.1], $D_x=1.593 \text{ g cm}^{-3}$ [1.553], $\text{Mo K}\alpha$, $\lambda=0.71073$ Å,

$\mu=9.278 \text{ cm}^{-1}$ [9.025], $F(000)=228$, $R=0.0349$ [0.0378], $wR=0.0472$ [0.0506] for 1222 [1074] reflections with $I \geq 3\sigma(I)$. The thermal motion of 1,3,5-trichloro-2,4,6-trimethylbenzene (or TCM) is rather high; no disorder can be detected in the range 150–297 K and X-rays provide information on H atoms. The quantum chemistry program AM1 gives a molecular conformation in reasonable accordance with