THE STRUCTURE OF THE AMIDE GROUP

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THE STRUCTURE OF THE AMIDE GROUP IN *p*-BROMOBENZOYLETHYLENIMINE

(Presented by Academician N. V. Belov, 19 VIII 1966)

The planar structure of the ordinary amide group is explained by amide resonance (^{1})

$$\mathrm{R{-}C(=O){-}N(R)R} \longleftrightarrow \mathrm{R{-}C({-}O^-){=}N^+(R)R}$$

In the presence of steric hindrances to a planar structure, amide resonance is forbidden, formation of the amide is made difficult, and the amide bond is weakened. This case is described by Bredt' s rule (^{2}), which forbids amide resonance in bridged systems with the nitrogen atom at the head of the bridge. Similar hindrances to amide resonance are observed in β-lactams.

We consider a new case of prohibition of amide resonance with a nitrogen atom included in a three-membered ring. Earlier, one of us presented some data in favor of such an effect (^{3}); however, unambiguous proof can be obtained only from exact knowledge of the geometry of the system.

For an X-ray structural study, *p*-bromobenzoylethylenimines (A) and *p*-bromobenzoyldimethylamine (B) were synthesized by acylation of the corresponding amines with *p*-bromobenzoyl chloride.

Compound A: m.p. 55.5-56.5°.

C_9H_8NOBr.	Found, %:	C 47.70; H 3.62; N 6.14
	Calculated, %:	C 47.82; H 3.57; N 6.20

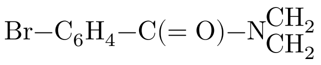
IR spectrum: $\nu_{C=O} = 1665\ \mathrm{cm}^{-1}$; NMR spectrum: $\delta_{\Delta N-} = 2.28$ ppm; A_2B_2 multiplet from the protons of the benzene ring, $\delta = 7.70$ ppm.

Compound B: m.p. 72-74°.

$C_9H_{10}NOBr$.	Found, %:	C 47.31; H 4.43; N 6.19
	Calculated, %:	C 47.39; H 4.42; N 6.14

IR spectrum: $\nu_{\mathrm{C=O}} = 1625\ \mathrm{cm}^{-1}$; NMR spectrum: $\delta_{(\mathrm{CH3})_2\mathrm{N}-} = 2.90$ ppm; A_2B_2 multiplet from the protons of the benzene ring, $\delta = 7.38$ ppm relative to the signal from hexamethyldisiloxane.

The experimental X-ray diffraction material was obtained with Cu radiation and consists of a set of Weissenberg photographs. In all, 507 independent reflections with $F_\vartheta \neq 0$ out of 630 possible were recorded for A, and 555 reflections out of 600 possible for B. The intensities of the reflections were estimated visually. For both compounds the following basic crystallographic data were obtained:

(A) 

$$\mathrm{Br{-}C_6H_4{-}C(=O){-}N}\begin{matrix}\mathrm{CH_2}\\ \mathrm{CH_2}\end{matrix}$$

, (B) $\mathrm{Br{-}C_6H_4{-}C(=O){-}N(CH_3)_2}$

A: $a = 10,76 \pm 0,03$ Å; $b = 10,21 \pm 0,05$ Å; $c = 8,42 \pm 0,01$ Å; $\alpha = \beta = \gamma = 90°$; $V = 925$ $\mathrm{\AA}^3$; $d_{\mathrm{meas}} = 1,66\ \mathrm{g/cm}^{-3}$; $d_{\mathrm{rent}} = 1,65\ \mathrm{g/cm}^{-3}$; $F(000) = 448$; $M = 226,087$; $Z = 4$; $\mu = 63\ \mathrm{cm}^{-1}$ $(\mathrm{Cu}K_\alpha)$.
B: $a = 13,87 \pm 0,04$ Å; $b = 9,84 \pm 0,01$ Å; $c = 7,12 \pm 0,01$ Å; $\alpha = \beta = \gamma = 90°$; $V = 972$ $\mathrm{\AA}^3$; $d_{\mathrm{meas}} = 1,58\ \mathrm{g/cm}^{-3}$; $d_{\mathrm{rent}} = 1,57\ \mathrm{g/cm}^{-3}$; $F(000) = 456$; $M = 228,103$; $Z = 4$; $\mu = 60\ \mathrm{cm}^{-1}$ $(\mathrm{Cu}K_\alpha)$.

Systematic extinctions of reflections indicated two possible space groups of symmetry, $Pnma$ and $Pn2_1a$, for A and B. In the case of the centrosymmetric group $Pnma$, with $Z = 4$, the molecules would have had to be located in mirror planes of symmetry. We considered this unlikely and adopted the group $Pn2_1a$ for both compounds. The subsequent course of the structure investigation confirmed this symmetry group. The structures were solved by the heavy-atom method. Refinement of the structures was carried out by the least-squares method (LSM) in several cycles using weighting schemes (^{4}). During refinement, corrections for secondary extinction, calculated from equation (^{5}), were introduced for some strong reflections,

Fig. 1. Bond lengths and valence angles in structure A of *n*-bromobenzoylethylenimine

$$K|F_{\mathrm{e}}| = |F_{\mathrm{B}}| \exp[-vI_{\mathrm{B}}], \quad \text{where} \quad I_{\mathrm{B}} = F_{\mathrm{B}}^2 LP.$$

For structure B, after refinement the final $R = 11,7\%$. The noticeable scatter in the bond lengths of the benzene ring in structure A made it necessary to carry out for it a final LSM cycle according to Waser (^{6}). At first, as an additional condition, all bond lengths in the benzene ring were constrained to the mean value 1, 41 Å; then this condition was replaced by the condition that all these bonds be equal to one another. As a result of this refinement, the overall R-factor for all reflections (including zero reflections with $F_{\mathrm{e}} = \frac{1}{2}F_{\min}$) did not change (10,7%), but the R'-factor, calculated only for the light atoms after subtracting the Br contribution from $|F_{\mathrm{e}}|$, decreased from 19 to 17,4%.

Table 1

Atoms	A: x/a	A: y/b	A: z/c	A: B_j, Å^2	A: ρ, el/Å^3	B: x/a	B: y/b	B: z/c	B: B_j, Å^2	B: ρ, el/Å^3
Br	0,1827	1,0000	0,1421	−6,57	38,8	0,7816	0,5000	0,9460	−5,83	43,7
C (1)	0,2049	0,8107	0,1411	−7,60	4,0	0,6977	0,4867	0,7409	−3,88	6,3
C (2)	0,1238	0,7311	0,0532	−4,41	5,0	0,6990	0,5846	0,5948	−3,82	6,1
C (3)	0,1389	0,5945	0,0550	−5,47	4,6	0,6362	0,5733	0,4350	−4,95	5,5
C (4)	0,2397	0,5388	0,1365	−5,34	4,6	0,5764	0,4610	0,4304	−2,82	7,0
C (5)	0,3302	0,6199	0,2049	−4,09	4,9	0,5708	0,3650	0,5767	−4,49	5,9
C (6)	0,3108	0,7557	0,2122	−4,51	4,9	0,6359	0,3758	0,7294	−4,89	5,8
C (7)	0,2636	0,3971	0,1227	−3,42	5,3	0,4989	0,4607	0,2823	−4,16	6,4
C (8)	0,4867	0,3642	0,0612	−4,68	4,9	0,5391	0,2193	0,1850	−4,18	5,4
C (9)	0,4270	0,2318	0,0802	−4,76	4,5	0,3975	0,3426	0,0283	−5,38	5,3
N	0,3793	0,3464	0,1702	−5,57	6,0	0,4777	0,3477	0,1776	−3,11	8,0
O	0,1755	0,3165	0,1052	−7,52	6,0	0,4583	0,5700	0,2378	−4,22	8,7

Table 1 gives the final values of the atomic coordinates, the individual isotropic temperature corrections B_j, and the heights of the electron-density maxima ρ for structures A and B. According to these coordinates, zero difference syntheses were constructed. In the character of the electron-density distribution in these syntheses, the anisotropy of the thermal vibrations of the Br atom, which we did not take into account, was clearly manifested.

The maximum peak height in the difference syntheses in both structures was $\sim \pm 1.5$ e/Å^3.

The errors in determining the atomic coordinates, calculated by the formulas of B. K. Vainshtein—A. M. Porai-Koshits (^{7,8}), are: $\varepsilon(\mathrm{Br}) = \pm 0.002$ Å; $\varepsilon(\mathrm{C}) = \pm 0.015$ Å; $\varepsilon(\mathrm{N}) = \pm 0.01$ Å; $\varepsilon(\mathrm{O}) = \pm 0.01$ Å. The accuracy in determining valence angles, calculated by Darlow's formulas (^{9}), is $\pm 1^\circ 30'$, and the maximum standard deviation in determining interatomic distances is $\Delta r_{\mathrm{C-C}} = \pm 0.02$ Å.

In Fig. 1 the interatomic distances and valence angles in structure A are given. The angle between the plane of the ethylenimine ring and the C(7)—N bond is

122°03′. The plane of the carbonyl group C(4)C(7)ON is rotated relative to the plane of the benzene ring by an angle of 18°27′. The interatomic distance

$$\mathrm{C(4)—C(7)} = \mathrm{C}_{sp^2}—\mathrm{C}_{sp^2} = 1.47\ \text{Å}$$

is appreciably shorter than the single bond

$$\mathrm{C}_{sp^3}—\mathrm{C}_{sp^3} = 1.54\ \text{Å}.$$

This is explained by two effects: conjugation and an increase in the *s*-character of this bond (10).

Fig. 2. Bond lengths and valence angles in structure B of *n*-bromobenzoyldimethylamine

The interatomic distances and valence angles in structure B are given in Fig. 2. The mean interatomic distance $\mathrm{C}_{ar}—\mathrm{C}_{ar}$ is 1.41 Å. The bond lengths $\mathrm{C}_{sp^2}—\mathrm{N}$, 1.37 Å, and $\mathrm{C} = \mathrm{O}$, 1.25 Å, in the amide group agree well with analogous interatomic distances in other amides (1,11).

Fig. 3. Bond orders and charge distribution in *n*-bromobenzoyldimethylamine

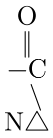
The amide group itself is only approximately planar: the plane C(7)NC(8)C(9) is rotated relative to the plane of the carbonyl group C(4)C(7)ON by 9°18′. The plane of the carbonyl group forms an angle of 45°30′ with the plane of the benzene ring. These rotations of the planes relative to one another are caused by steric hindrance.

Molecule B was calculated by us by the simple molecular-orbital method in the π-electron approximation (12,13). In Fig. 3 the bond orders and charge distribution are given.

The results obtained by the Hückel method agree well with the results of the structural investigation.

Thus, the X-ray structural study has proved the pyramidal structure of nitrogen in the ethyleneamide group (pyramid height 0.65 Å). From the data obtained one may conclude that amide resonance is forbidden at a nitrogen incorporated into a three-membered ring.

The shift of the frequency of the valence vibrations of the carbonyl group, $\Delta\nu = 40\ \mathrm{cm}^{-1}$, and the high frequency of nitrogen inversion in A are analogous to those of other N-acylethylenimines studied[3]; therefore the structure obtained may be regarded as common to the ethyleneamide group:



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[1] L. Pauling, R. B. Corey, *Proc. Nat. Acad. Sci. U.S.A.*, **37**, 729 (1953).
[2] F. S. Fawcett, Chem. Rev., **47**, 249 (1950).
[3] R. P. Shibaeva, L. O. Atovmyan, R. G. Kostyanovskii, VII International Congress and Symposium on Crystal Growth. Abstracts of Reports. VIII, 89, "Nauka," 1966, p. 121.
[4] *Computing Methods and Phase Problem in Crystal Analysis*, Glasgow, 1961, pp. 45–46.
[5] P. R. Pinnock, C. A. Taylor, H. Lipson, Acta Cryst., **9**, No. 2, 173 (1956).
[6] J. Waser, Acta Cryst., **16**, No. 11, 1091 (1963).
[7] B. K. Vainshtein, *JETP*, **27**, issue 1 (1954).
[8] M. A. Porai-Koshits, *Practical Course in X-ray Structure Analysis*, Moscow, 1961.
[9] C. F. Darlow, Acta Cryst., **13**, 6, 683 (1960).
[10] M. Dewar, *Hyperconjugation*, Moscow, 1965.
[11] M. Hospital, J. Housty, Acta Cryst., **20**, 3, 368 (1966).
[12] J. Roberts, *Calculations by the Method of Molecular Orbitals*, IL, 1963.
[13] B. Pullman, A. Pullman, *Quantum Biochemistry*, IL, 1965.

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