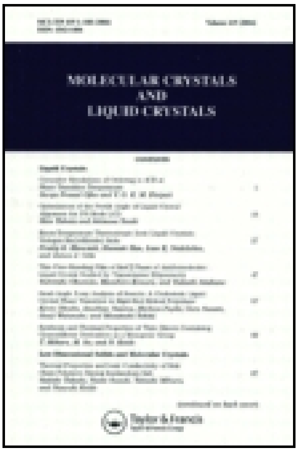

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Precision X-ray Diffraction Study of the Secondary Interactions in the Crystal of 1-Dimethylcarbamoyl-8-Dimethylaminonaphthalene

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Precision X-Ray Diffraction Study of the Secondary Interactions in the Crystal of 1-Dimethylcarbamoyl-8-Dimethylamino-naphthalene

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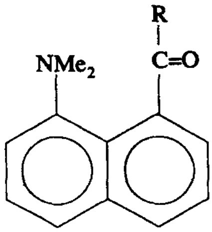
X-ray diffraction method has been used to study the structure and electron density distribution in the crystal of 1-dimethylcarbamoyl-8-dimethylaminonaphthalene. Attractive interaction between a nucleophilic nitrogen atom and an electrophilic carbon atom has been established. These atoms are at a distance of 2.71 Å which is much less than the sum of the Van der Waals radii (3.25 Å). A number of specific features in the deformation electron density maps are accounted for by this interaction. Comparative analysis of the structural features of the compound studied (along with theoretical calculations by MMP2 and MNDO methods) and a number of other naphthalene perisubstituted derivatives confirms the presence of the attractive interaction.

Keywords: X-ray diffraction, electron density distribution

1. INTRODUCTION

It was found earlier (Ref. 1) for a series of perisubstituted naphthalene derivatives I–III that substituents



I: $R=CH_3$
II: $R=OH$
III: $R=OCH_3$
IV: $R=NMe_2$

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in positions 1 and 8 of the naphthalene nucleus are at much shorter distances than the sum of the Van der Waals radii, which favors nonbonded intramolecular interaction between electrophilic and nucleophilic substituents. It might be expected that this interaction would stabilize the molecular conformations strongly preferred for its realization. The geometry of these compounds may be intermediate, corresponding to the formation of the chemical bond between nucleophilic and electrophilic centers in the process of nucleophilic addition to the carbonyl group.

To study in detail the specific features of these interactions, a precise X-ray diffraction study of 1-dimethylcarbamoyl-8-dimethylaminonaphthalene (IV) has been carried out and quantum-chemical calculations for molecules I–IV characterized by favorable conditions for attractive interaction between an electrophilic carbon atom and a nucleophilic nitrogen atom were performed.

2. EXPERIMENTAL

An X-ray diffraction data collection was carried out at two temperatures for two different single crystal samples of IV: at room temperature, to obtain the structural model and at $T = 147$ K, to obtain the electron density distribution maps and precise structural parameters of the molecule.

Compound IV is crystallized as yellow monoclinic prisms. Crystallographic data at $T = 293$ K: $C_{15}H_{18}N_2O$, $M = 242.2$, $a = 12.202(5)$, $b = 13.813(4)$, $c = 8.766(5)$ Å, $\beta = 108.01(4)°$, $V = 1405$ Å^3, $Z = 4$, $d_{calc} = 1.146$ g/cm^3, space group $P2_1/a$. Intensities of 1204 independent reflections with $I > 3\sigma$ were measured on a "KM-4" diffractometer using MoK_α radiation. The structure was solved by the direct method using the package of SHELX programs and refined by the full-matrix least-squares technique in anisotropic approximation. Hydrogen atoms were revealed in the difference synthesis of the electron density and refined in isotropic approximation. The final R value was 0.036.

For a precision low-temperature study, a single crystal of prismatic form with dimensions 0.3*0.3*0.4 mm was chosen. X-ray diffraction data were obtained at 147 ± 2 K on the "Siemens $P3$/PC" diffractometer (MoK_α radiation, graphite monochromator, $\theta/2\theta$-scan, $2\theta < 100°$). Crystallographic data at 147 K: $a = 8.697(1)$, $b = 13.354(2)$, $c = 12.341(2)$ Å, $\beta = 108.03(2)°$, $V = 1362.9(7)$ Å^3, $Z = 4$, $d_{calc} = 1.181$ g/cm^3, space group $P2_1/C$. A total of 7276 reflections were measured (for $2\theta < 70°$ experimental data were obtained from reciprocal space hemisphere and for $70° < 2\theta < 100°$ one independent region was measured, divergence factor of the intensities of equivalent reflections $R_{int} = 0.018$). In further calculations 3690 observed independent reflections with $I > 3\sigma(I)$ were used. For structure refinement, atomic positions of the room temperature data (after applying the transformation from $P2_1/a$ to $P2_1/c$ space group) were used as the starting model. The structure was refined using the least-squares method in the full-matrix anisotropic (isotropic for H atoms) approximation to $R = 0.046$, $R_w = 0.048$, GOF = 1.63. Absorption and extinction corrections were neglected as they were found to be insignificant. At the final stages, a "quasi-high-angle" refinement with Dunitz-Seiler (Ref. 2) weighting scheme ($f = 1 - \exp[-B * \sin^2\theta/\lambda^2]$

with $B = 3.0\,\text{Å}^2$) was carried out using 2780 reflections with $\sin\theta/\lambda > 0.40\,\text{Å}^{-1}$. The results of this refinement: $R = 0.041$, $R_w = 0.042$, GOF = 1.09, H atom parameters were fixed. The deformation electron density (DED) maps were generated using reflections with $\sin\theta/\lambda < 0.70\,\text{Å}^{-1}$ with the structural model obtained in the high angle refinement. All calculations were performed on IBM PC/AT computer with the SHELXTL PLUS programs (Ref. 3).

Bond lengths and bond angles for molecule IV at room temperature and 147 K are listed in Tables 1 and 2, coordinates of non-hydrogen atoms and their isotropic thermal parameters (based on high angle refinement) at 147 K are given in Table 3.

3. RESULTS AND DISCUSSION

3.1 Molecular and Crystal Structure

A general view of molecule IV with atomic numbering is shown in Figure 1. The molecular structure at 147 K with the atomic representation as thermal ellipsoids (high angle refinement, $p = 50\%$) is shown in Figure 2.

The molecular structures of compounds I–IV are very similar. Bond lengths in the naphthalene moiety are in good agreement differing by no more than 0.01 Å for

TABLE 1

Bond Length and Bond Angles for Molecule IV at Room Temperature

Bond Length	Å	Bond Length	Å
C(1)–C(2)	1.379(3)	C(7)–C(8)	1.381(2)
C(1)–C(9)	1.432(2)	C(8)–C(9)	1.437(2)
C(1)–C(13)	1.513(3)	C(8)–N(1)	1.424(2)
C(2)–C(3)	1.410(3)	C(9)–C(10)	1.427(3)
C(3)–C(4)	1.367(3)	C(11)–N(1)	1.468(2)
C(4)–C(10)	1.424(3)	C(12)–N(1)	1.461(2)
C(5)–C(6)	1.368(2)	C(13)–N(2)	1.351(2)
C(5)–C(10)	1.420(3)	C(13)–O(1)	1.234(3)
C(6)–C(5)	1.368(2)	C(14)–N(2)	1.455(3)
C(6)–C(7)	1.412(2)	C(15)–N(2)	1.451(3)
C(2)C(1)C(9)	120.0(2)	C(1)C(2)C(3)	121.4(2)
C(2)C(1)C(13)	115.5(2)	C(2)C(3)C(4)	120.0(2)
C(9)C(1)C(13)	124.5(1)	C(3)C(4)C (10)	120.4(2)
C(6)C(5)C(10)	120.7(2)	C(1)C(13)N(2)	117.0(3)
C(1)C(13)O(1)	120.4(2)	C(8)N(1)C(11)	111.4(2)
N(2)C(13)O(1)	122.1(3)	C(8)N(1)C(12)	115.1(3)
C(5)C(6)C(7)	120.4(2)	C(11)N(1)C(12)	110.9(2)
C(6)C(7)C(8)	120.9(2)	C(13)N(2)C(14)	118.3(2)
C(7)C(8)C(9)	119.7(3)	C(13)N(2)C(15)	124.2(3)
C(7)C(8)N(1)	123.3(3)	C(14)N(2)C(15)	116.5(2)
C(9)C(8)N(1)	117.0(2)	C(4)C(10)C(5)	120.8(2)
C(1)C(9)C(8)	123.4(2)	C(4)C(10)C(9)	119.9(2)
C(1)C(9)C(10)	118.0(2)	C(5)C(10)C(9)	119.3(1)
C(8)C(9)C(10)	118.6(2)		

TABLE 2

Bond Length and Bond Angles for Molecule IV at $T = 147$ K

Bond Length	Å	Bond Length	Å
C(1)-C(2)	1.378(1)	C(7)-C(8)	1.381(2)
C(1)-C(9)	1.433(2)	C(8)-C(9)	1.438(1)
C(1)-C(13)	1.513(1)	C(8)-N(1)	1.424(2)
C(2)-C(3)	1.411(2)	C(9)-C(10)	1.424(1)
C(3)-C(4)	1.366(2)	C(11)-N(1)	1.463(2)
C(4)-C(10)	1.424(1)	C(12)-N(1)	1.467(2)
C(5)-C(6)	1.367(2)	C(13-N(2)	1.351(1)
C(5)-C(10)	1.418(2)	C(13)-O(1)	1.236(1)
C(6)-C(5)	1.367(2)	C(14)-N(2)	1.451(2)
C(6)-C(7)	1.410(2)	C(15)-N(2)	1.454(2)
C(2)C(1)C(9)	120.0(1)	C(1)C(2)C(3)	121.3(1)
C(2)C(1)C(13)	115.5(1)	C(2)C(3)C(4)	120.0(1)
C(9)C(1)C(13)	124.5(1)	C(3)C(4)C(10)	120.5(1)
C(6)C(5)C(10)	120.7(1)	C(1)C(13)N(2)	117.0(1)
C(1)C(13)O(1)	120.5(1)	C(8)N(1)C(11)	114.9(1)
N(2)C(13)O(1)	122.0(1)	C(8)N(1)C(12)	111.2(1)
C(5)C(6)C(7)	120.4(1)	C(11)N(1)C(12)	111.0(1)
C(6)C(7)C(8)	121.0(1)	C(13)N(2)C(14)	124.2(1)
C(7)C(8)C(9)	119.5(1)	C(13)N(2)C(15)	118.4(1)
C(7)C(8)N(1)	123.4(1)	C(14)N(2)C(15)	116.5(1)
C(9)C(8)N(1)	117.0(1)	C(4)C(10)C(5)	120.8(1)
C(1)C(9)C(8)	123.3(1)	C(4)C(10)C(9)	119.8(1)
C(1)C(9)C(10)	118.0(1)	C(5)C(10)C(9)	119.4(1)
C(8)C(9)C(10)	118.6(1)		

TABLE 3

Atom Coordinates ($*10^4$) and Isotropic Displacement Parameters ($\text{Å}^2 * 10^3$)

Atom	*X*	*Y*	*Z*	*U*
O(1)	7387(1)	890(1)	6435(1)	25(1)
N(1)	7094(1)	2076(1)	8562(1)	24(1)
N(2)	7386(1)	−170(1)	7866(1)	26(1)
C(1)	4933(1)	774(1)	6915(1)	18(1)
C(2)	3835(1)	275(1)	6033(1)	22(1)
C(3)	2154(1)	395(1)	5815(1)	26(1)
C(4)	1587(1)	970(1)	6524(1)	26(1)
C(5)	2105(2)	2032(1)	8240(1)	31(1)
C(6)	3157(2)	2522(1)	9140(1)	33(1)
C(7)	4827(2)	2534(1)	9272 (1)	28(1)
C(8)	5442(1)	2028(1)	8522(1)	22(1)
C(9)	4376(1)	1438(1)	7626(1)	19(1)
C(10)	2679(1)	1486(1)	7458(1)	23(1)
C(11)	8241(1)	2244(1)	9696(1)	43(1)
C(12)	7332(2)	2808(1)	7742(1)	31(1)
C(13)	6692(1)	535(1)	7083(1)	19(1)
C(14)	6666(2)	−565(1)	8693(1)	41(1)
C(15)	9068(2)	−429(1)	8036(1)	41(1)

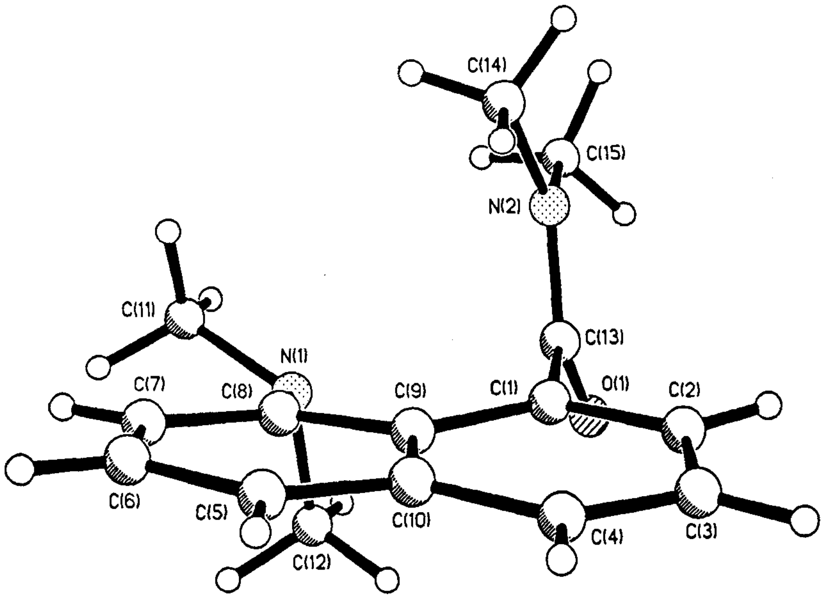


FIGURE 1 General view of molecule IV and atomic numbering.

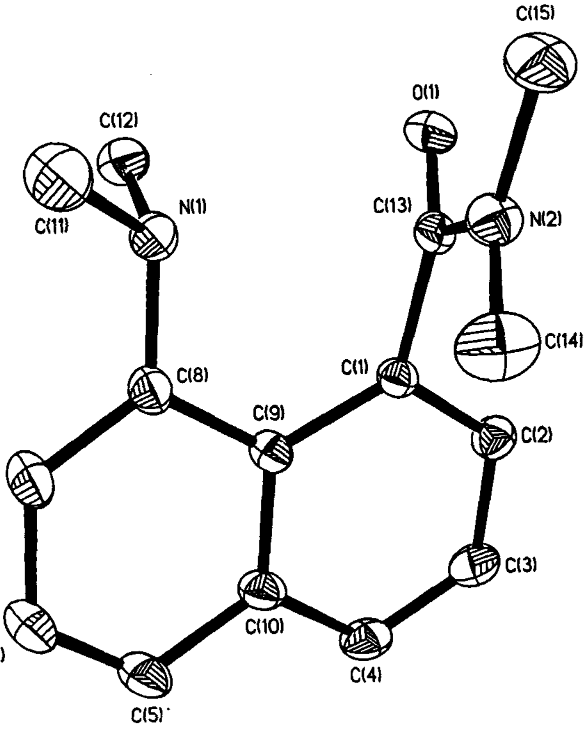


FIGURE 2 View of molecule IV with the atoms representation as ellipsoids of thermal vibrations (data at 147 K).

compounds I–IV. As compared with the unsubstituted naphthalene (the data from Ref. 4 at 100 K), in compound IV the C(1)–C(9) and C(8)–C(9) bond lengths adjacent to the substituents appear to be ~0.01 Å longer, and the C(5)–C(6) and C(3)–C(4) bond lengths are respectively shorter. The naphthalene moiety in IV is planar, the average displacement of C(1)–C(10) atoms from the mean plane is 0.046 (293 K) and 0.054 (147 K) Å. The largest displacement was found for C(1) and C(8) atoms (−0.06 and 0.08 Å at 293 K, −0.08 and 0.10 Å at 147 K). Deviations of atoms C(13) and N(1) from the same plane are even larger: −0.205 and 0.270 Å at 293 K and −0.271 and 0.298 Å at 147 K respectively. One possible reason for the latter deviation is the repulsion between the substituents in 1- and 8-positions. An analogous tendency is also observed for structures I–III: the deviation of atom C(13) from the mean plane of the naphthalene moiety is −0.11, −0.15 and −0.24 Å, and that of N(1) is 0.10, 0.17 and 0.29 Å respectively.

In molecules I–IV both substituents are non-coplanar with the naphthalene fragment plane. The rotation angles of the dimethylamino group (α) and the carbonyl group (β) with respect to the naphthalene moiety are close to 90° (Table 4, in which some significant geometrical parameters of molecules I–IV are compared). The rotation of the substituents in the peri-positions is due to steric factors. This is confirmed by the presence of short non-bonded intramolecular distances. For instance, in IV (at 147 K) the distance O(1)...C(12) is equal to 3.034(2) Å, O(1)...N(1) 3.143(2) Å, and N(1)...N(2) 3.152(2) Å.

The nitrogen atoms of the dimethylamino groups in I–IV have a pyramidal configuration. The sum of the bond angles Σ_N and the displacement δ_N of the N(1) atom from the plane through its three bonded atoms towards the acyl substituent are in the range of 337–340° and 0.39–0.41 Å.

This structural feature of molecules I–IV provides favorable conditions for attractive interactions between the nucleophilic N(1) atom of the dimethylamino substituent and the electrophilic C(13) atom of the acyl substituent. Assuming that the lone pair

TABLE 4

Comparison of some Geometrical Parameters of I–IV

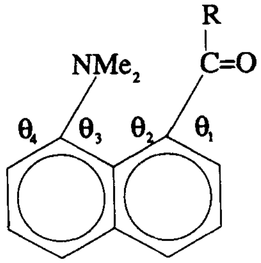
Compound	I	II	III	IV
R	CH_3	OH	OCH_3	$N(CH_3)_2$
α, deg	75	79	77	61 (64)*
β, deg	73	73	85	78 (76)
γ, deg	104	102	99	99 (99)
Σ_N, deg	337	340	338	337 (339)
δ_N, Å	0.40	0.39	0.40	0.41 (0.39)
Δ, Å	2.56	2.61	2.59	2.70 (2.71)
δ_C, Å	0.088	0.061	0.062	0.056 (0.055)
θ_1, deg	117.2	116.3	118.5	115.5 (115.4)
θ_2, deg	123.2	123.9	121.6	124.5 (124.7)
θ_3, deg	116.6	117.4	117.4	117.1 (117.6)
θ_4, deg	123.4	123.0	123.6	123.3 (122.1)
$d(1\ldots8)$, Å	2.49	2.49	2.51	2.53 (2.52)

* In brackets are given data at 147 K. All other data—at room temperature.

electrons (L_p) of the N(1) atom complement its configuration to the ideal tetrahedral, this L_p will be directed approximately towards the carbonyl C(13) atom. Deviation of this idealized L_p orientation from the N...C line in I–IV is in the range of 15–24°. The intramolecular non-bonded distances (Δ) are shortened to 2.56–2.71 Å as compared with the sum of the Van der Waals radii of the N and C atoms (3.21 Å) (Ref. 5)).

The specific distortion of the bond angles at C(1) and C(8) atoms (that are also compared in Table 4) is a characteristic feature of the compounds of the examined series.

In all compounds I–IV, the exocyclic angles θ_2 and θ_4 appear to be more than 120°. Thus, in the naphthalene plane the bonds with the substituents are displaced from idealized directions to one side, as distinct from most of the structurally studied 1,8-disubstituted naphthalene derivatives, in which these bonds are displaced to opposite sides both in the plane of naphthalene and perpendicular to it, as mentioned in Ref. 1. The observed distortions of the exocyclic bonds in I–IV might be attributed to the non-bonding N...C interactions. There is some evidence that the most favorable conditions for a carbonyl group attack by a nucleophile (Nu) appear at Nu...C=O angle (γ) of 100–110° (Ref. 1, 6). The magnitude of this angle (Table 4) is determined by the nucleophilic properties of Nu as well as by those of the group bonded to the carbonyl carbon atom. It is expected that the molecular geometry of such compounds would "adjust" itself to these conditions. However, since the decreasing angle γ in the studied series leads to increasing Nu...C distance (Ref. 1), the observed molecular goemetry should be simultaneously determined by the demand for minimal Nu...C distance and optimal value of γ. These effects along with steric repulsion should evidently account for the observed orientation of the exocyclic bonds.



Another indication of an attractive interaction between the two perisubstituents is the displacement of the carbonyl carbon atom (δ_c) from the plane through the atoms bonded to it, towards the nucleophilic center. Because of the structural similarity of the investigated molecules it is natural to expect that the δ_c should depend on the electrophilic property of the carbonyl carbon atom COR > COOH ~ COOR > CO—NR$_2$). In the series I–IV the δ_c value actually increases in the indicated sequence: 0.088 > 0.061 ~ 0.062 > 0.056 Å. Steric factors may also affect the δ_c value.

The N(2) atom in IV has a slightly pyramidal configuration (the sum of the bond angles is equal to 359.0°) and is displaced by 0.080 Å from the plane of the bonded atoms in the opposite direction to the displacement of the carbonyl carbon atom. This structural feature of the CO—NMe$_2$ substituent was observed elsewhere (Ref. 1) and is in agreement with the stereo-electronic effects on the breakdown of the tetrahedral intermediate formation in the hydrolysis of esters and N-disubstituted imidates (Ref. 7).

To sum up, a number of structural features of molecules I–IV confirm the existence of attractive interaction between the carbonyl carbon atom of the substituent in position 1 and the nucleophilic nitrogen atom of the substituent in position 8 of the naphthalene moiety. The most significant of these features are: the shortened C...N distance, the characteristic orientation of the exocyclic bonds, and the displacement of the carbonyl carbon atom from the plane through the atoms bonded to it towards the nucleophilic substituents which increases with the electrophilic property of the COR substituent.

3.2 Thermal Motion in the Crystal

An analysis of the anisotropic atomic displacement parameters in structure IV was carried out using the LTS-model of the rigid body (Ref. 8). As a whole, molecule IV is not rigid as evidenced, in particular, by poor agreement between the calculated and the experimental anisotropic atomic displacement parameters ($R_u = 0.145$). The reason for the intramolecular non-rigidity is evidently due to the rotational vibrations of the dimethylamino and acyl groups around C(8)–N(1) and C(1)–C(13) bonds. This is also qualitatively confirmed by the shape of the thermal ellipsoids of the corresponding atoms (Fig. 2). On the contrary, the naphthalene moiety of molecule IV is rigid: $R_u = 0.023$, the calculated libration corrections to bond lengths do not exceed 0.002 Å. The calculated *T*- and *L*- tensors are close to isotropic.

The calculated differences (*D*) of the projections of the mean-square displacements of pairs of atoms in the direction of the chemical bonds between them (Hirshfeld's rigid-bond postulate (Ref. 9)) confirm that the chemical bonds in molecule IV are rigid: the mean value of *D* is equal to 0.0005(3) Å for all pairs of chemically bonded atoms. The *D* values for pairs of chemically non-bonded atoms are, on the contrary, much greater. The pairs including the atoms of the Me-groups are characterized by the largest *D* values. This result is an additional confirmation of the structural non-rigidity of molecule IV as a whole, which is shown by the intramolecular oscillations of the dimethylamino and acyl groups.

3.3 Electron Density Distribution

To study the electron density distribution in the region of the N...C intramolecular interaction in question, the deformation electron density (DED) maps were generated and analyzed in different sections of molecule IV.

A section through the mean plane of the naphthalene moiety is shown in Figure 3. The DED maxima are very distinct in the midpoints of the C—C bonds, as well as in the C—H bonds. The positions of these peaks, their shapes and heights are close to that obtained for naphthalene (Ref. 4).

Especially interesting is the region between N(1) and C(13) atoms. The DED section through the atoms C(13), N(1), and N(2) is represented in Figure 4. The L_p of the nucleophilic nitrogen atom N(1), as well as the DED peak on the C(13)–N(2) bond, are distinctly seen in this figure. The last peak is significantly extended along the direction

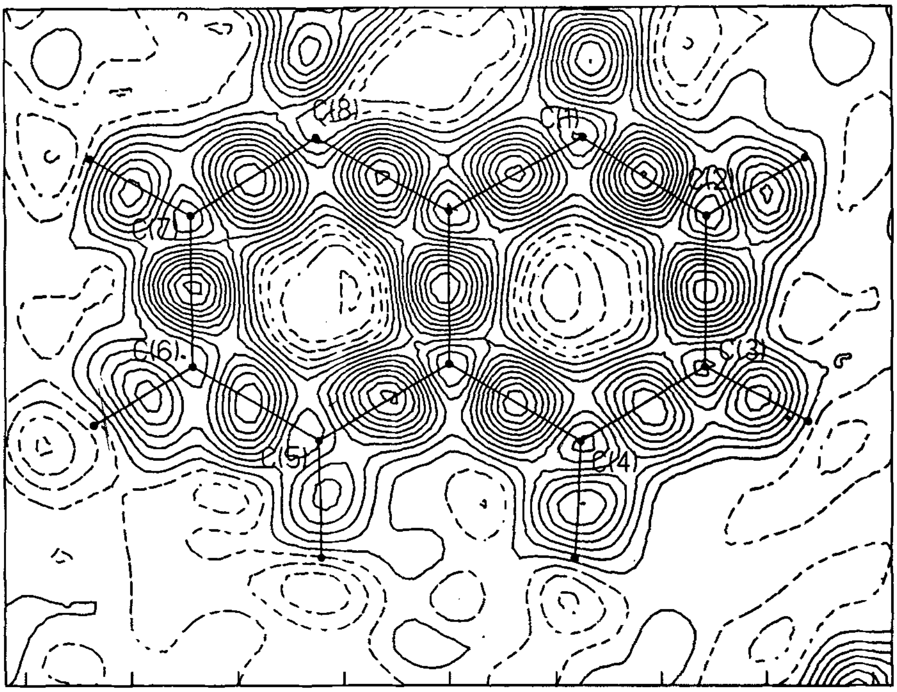


FIGURE 3 DED section in the mean plane of molecule IV naphthalene moiety. In this and other figures isolines are drawn through 0.05 e/Å^3, the negative DED lines are dashed.

perpendicular to the bond, i.e. it has a pronounced π-component, as a result of conjugation in the N(2)–C(13)=O(1) amide group. Essential amide conjugation is also confirmed by significant shortening of the C(13)–N(2) bond to 1.350(1) Å.

To determine the direction of the N(1) L_p, DED sections were made at various distances (d) from the N(1) nitrogen atom in the planes perpendicular to the idealized direction of the L_p of this atom, assuming its sp^3-hybridization (i.e. idealized tetrahedral environment of N(1), including its L_p). Such sections allow us to establish the displacement of the nitrogen L_p maximum induced by its non-bonded environment. At $d = 0.6$ Å (the distance corresponding to L_p peak maximum), the L_p direction coincides with the idealized one. Further, at $d = 0.6$–1.0 Å, the L_p direction is slightly splaying within one contour (0.05 e/Å^3), but as a whole its idealized direction is preserved. It should be noted that the N(1) atom L_p is directed towards the C(13)–N(2) bond rather than to the carbonyl atom C(13).

The DED section in Figure 5 is made through the atoms N(1), C(13), and the idealized direction (see above) of the N(1) atom L_p. The displacement of the N(2) atom from the section plane is 0.4 Å. In this section the displacement of the DED peak from C(13)–N(2) bond towards the N(1) atom L_p is observed. This displacement is also observed in Figure 4, as well as in the midsection perpendicular to the C(13)–N(2) bond, indicating certain "bending" of the C(13)–N(2) bond and shortening of the distance between the peak of this bond and N(1) atom L_p.

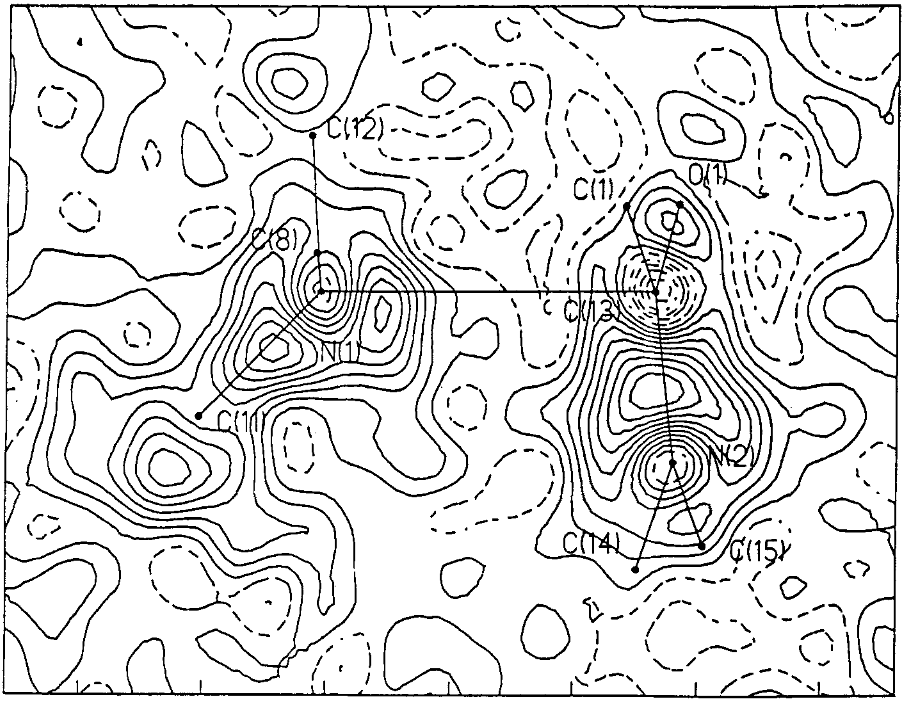


FIGURE 4 DED section in the plane of C(13), N(1) and N(2) atoms.

An interesting pattern of the DED distribution is observed in the region of the C(13)=O(1) bond. In Figure 6 the DED section through C(13) and O(1) atoms perpendicular to the mean plane of the carbonyl atom bonds is presented. The DED peak is very distinct on the C(13)–O(1) bond, having a powerful π-component. This peak is slightly displaced from the bond in the direction opposite to the N(1) atom L_p peak. The C=O bond "bending" is assumed to be connected with the repulsion between the C=O bond electrons and the nitrogen atom L_p.

Therefore, a number of characteristic features on the DED maps may be accounted for by the interaction in question. First, it is the shortening of the distances between the DED peaks, one of which corresponds to the N(1) atom L_p, and the other is located in C(13)–N(2) bond. The DED maximum between C(13) and N(2) atoms is displaced from the C(13)–N(2) bond. The direction of the N(1) atom L_p is obviously determined by this interaction. The indicated shortening of the distance between the DED peaks may be explained in terms of the attractive interaction between C(13) and N(1) atoms, in which the n-orbitals of N(1) and N(2) and the π-orbital of the C=O bond may take part. It should be noted that while the DED peak in the C(13)–N(2) bond is displaced to the N(1) atom L_p, the DED peaks in the bonds C(13)= O(1) (Fig. 6) and C(13)–C(1) (Fig. 5) are displaced away from it, which is in agreement with the electrostastic repulsion of the electron density peaks without interaction between them that is caused by the superposition of the orbitals.

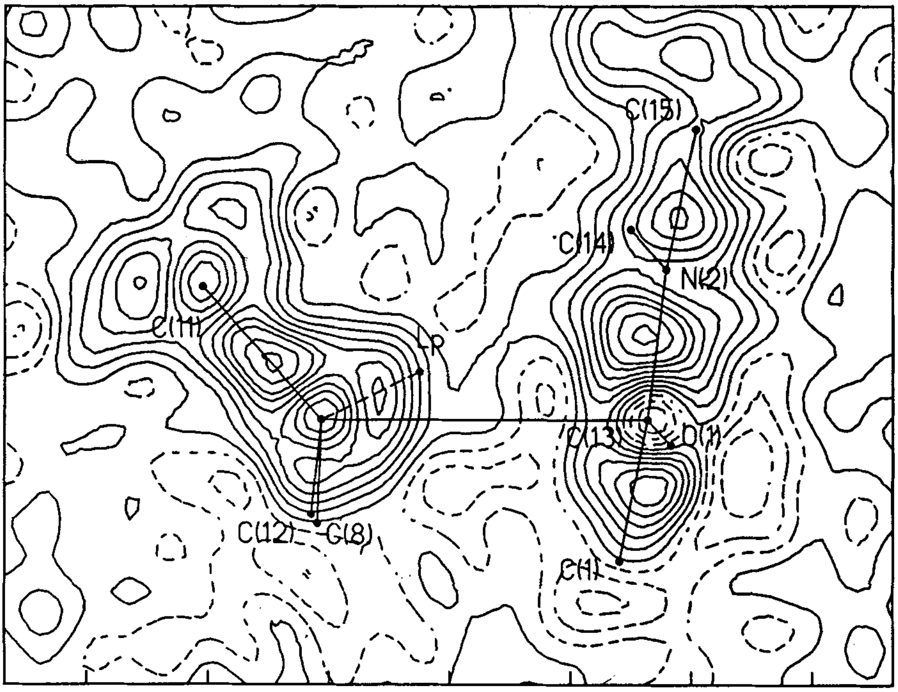


FIGURE 5 DED section in the plane of C(13), N(1) atoms and through the maximum of DED peak corresponding to N(1) lone pair electrons.

Thus, it may be assumed that in case of compound IV the N(1) L_p interacts with the elctron density localized on the C(13)–N(2) bond, i.e. the interaction has a three-center character. It is apparently connected with the "amide" conjugation of the N(2) L_p with the π-orbital of the carbonyl group, leading to delocalization of its electron density to the C(13)–N(2) bond. As the π-donor properties of the R substituents are weakened throughout compounds IV–I, the electron density is more localized on the C=O bond. As this takes place, the idealized L_p direction of the nucleophilic N(1) atom in compounds I–III is less displaced (15–17°) from the direction of the line between interacting atoms C(13) and N(1) than in compound IV (24° at $T = 293$ K, 26° at $T = 147$ K). This result supports the idea that the L_p direction of the nucelophilic nitrogen atom in the considered compounds is determined by attractive interactions. Actually, in IV, where the electron density is displaced towards the C(13)–N(2) bond, the N(1) L_p is directed approximately to this bond. In compounds I–III where there is no amide conjugation, and electron density displacement should not exist, the idealized direction of the N(1) atom L_p is displaced towards the carbonyl carbon C(13) atom. These effects influence the preferred direction of the nucleophilic attack to the electrophile, changing the most favorable attack angle (N....C=O), thus affecting the orientation of the exocyclic bonds.

For further study of non-bonded interactions discussed in this paper, the investigation of the character of the DED distribution in compounds I–III is of essential interest.

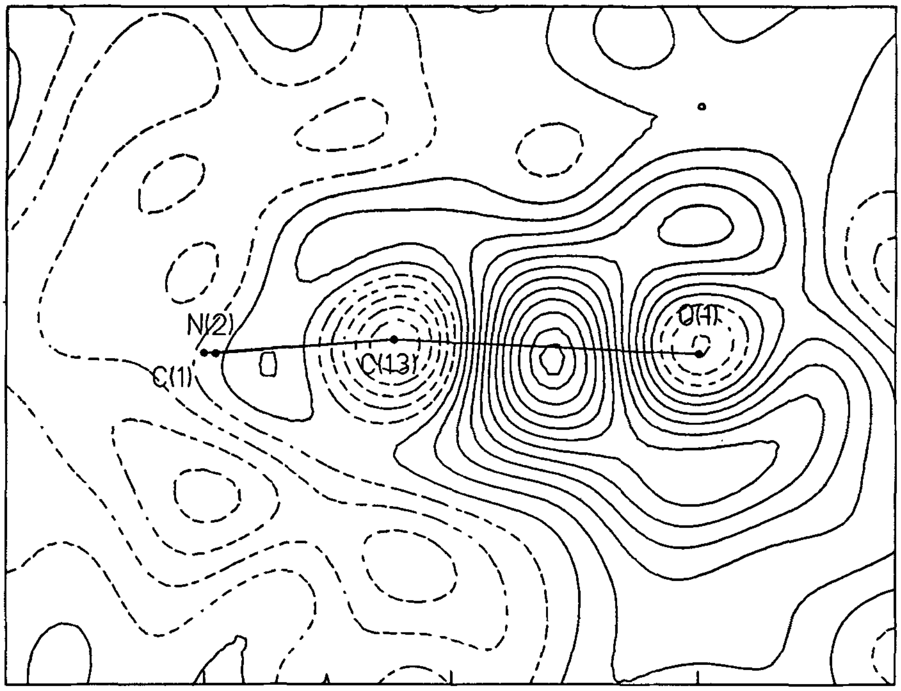


FIGURE 6 DED section through atoms C(13) and O(1) normal to the mean plane through C(13) and bonded to it atoms.

3.4 Theoretical Calculations

The value of δ_c, i.e. the displacement of the carbonyl carbon atom from the plane of the atoms bonded to it, may be affected not only by the electrophilic property of this atom but also by various steric factors. To estimate the influence of the steric factors on the molecular structure, optimization of the molecular geometry of compounds I–IV was carried out using molecular mechanics method (MMP2 program) (Ref. 10). This method reproduces well non-bonded Van der Waals interactions, caused by steric effects, but ignores specific non-bonded interactions caused by superposition of molecular orbitals. As a result of such optimization, the "refined" structures I–IV differed only slightly from those obtained from the x-ray data. However, the characteristic structural features indicating the non-bonded N....C interactions were practically not reproduced. Thus, in accordance with the calculations, the displacement δ_c of the carbonyl carbon atom from the plane through its neighbours in molecules III and IV was absent, while in I and II it was lowered to 0.01 Å; the exocyclic angles $\theta_1 - \theta_4$ have approached the "natural" value of 120°; the exocyclic bonds in III were found to be bent to the opposite sides in the naphthalene moiety plane. Therefore, it is impossible to reproduce the above molecular structure features of the components studied by taking into account only steric factors.

To account for orbital interactions in the series of the compounds studied, calculations of their electron structure using the semi-empirical MNDO method (Ref. 11) were made. The results of these calculations were used to find the partial interaction energy (E_{int}) between the carbonyl carbon atom and the nitrogen atom of the second substituent. The main idea of this technique is using the Hartree-Fock-Roothaan equation for electronic energy E:

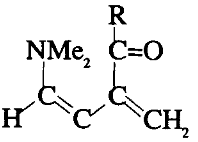
$$E = \sum_i \sum_j P_{ij}[H_{ij} + F_{ij}]/2 = \sum_i \sum_j E_{ij}^{AO}$$

where P_{ij} is the density matrix, H_{ij} is the core matrix (influence of non-valent electrons and an electron-nuclear interaction), F_{ij} is the Fock matrix (electron-electron interaction) and E_{ij}^{AO} is the pair electronic energy of interaction between atomic orbitals. Here

$$P_{ij} = 2 \sum_k^{N/2} C_{ik} C_{jk}; \quad \psi_i = \sum C_{ik} \Phi_k$$

where ψ_i is the molecular orbital, Φ_k is the atomic orbital and C_{ik} is the probability amplitude of the ψ_i localization on Φ_k. The matrix elements F_{ij}, H_{ij}, and P_{ij} were calculated with the semi-empirical MNDO method.

Further on we have carried out a summation of E_{ij}^{AO} which correspond to the atomic orbitals localized on the pairwise different atoms. Thus, we have obtained the partial energy components of the atom-atom interactions. Because of software limitations the calculations have been carried out on model molecules:



V: R=CH$_3$; VI: R=OH
VII: R=OCH$_3$
VIII: R=NMe$_2$

Results of the calculations of the energy E_{int} are given in Table 5, together with other values correlating with the electrophilic property of the COR substituent. The molecular structure of the compounds in question after full optimization of the molecular geometry using the MNDO method is qualitatively identical to the structure obtained with the x-ray method. In particular, the quantum chemical calculation reproduces displacement of the carbonyl carbon atom from its coordination plane towards

TABLE 5

Characteristics of attractive interaction in model molecules V–VIII

Compound	V	VI	VII	VIII
R	CH$_3$	OH	OCH$_3$	N(CH$_3$)$_2$
Δ, Å	2.56	2.61	2.59	2.71
δ_C, Å	0.088	0.061	0.062	0.055
$E_{\text{int, ev}}$	−0.215	−0.186	−0.184	−0.098

the dimethylamino substitutent. It is therefore expected that energy calculations qualitatively reproduce the non-bonded interaction studied. Table 5 shows that the partial energy E_{int} reflects the attractive character of this interaction and increases with the increasing electrophilic property of the COR substituent. Of course, these calculations cannot quantitatively reproduce the observed effects. However, they make it possible to identify the above-mentioned details of the structure with the interaction under study.

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