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265. Structural Studies of 1,8-Disubstituted Naphthalenes as Probes for Nucleophile-Electrophile Interactions[1])

by **W. Bernd Schweizer, Garry Procter**[2]), **Menahem Kaftory**[3]) and **Jack D. Dunitz**

Organic Chemistry Laboratory, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich

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Summary

Results of crystal structure analyses of seven 1,8-disubstituted naphthalenes (**2a**, 8-(*N, N*-dimethylamino)-1-naphthyl methyl ketone; **2b**, 8-(*N, N*-dimethylamino)naphthalene-1-carboxylic acid; **2c**, methyl 8-(*N, N*-dimethylamino)naphthalene-1-carboxylate; **2d**, 8-methoxy-1-naphthyl methyl ketone; **2e**, 8-methoxynaphthalene-1-carboxylic acid; **2f**, *N, N*-dimethyl-8-methoxynaphthalene 1-carboxamide; **2g**, *N, N*-dimethyl-8-hydroxynaphthalene-1-carboxamide) with a nucleophilic centre ($N(CH_3)_2$, OCH_3, OH) at one of the *peri* positions and an electrophilic centre (carbonyl C) at the other are described. All seven molecules show a characteristic distortion pattern: the exocyclic bond to the electrophilic centre is splayed outward, and the one to the nucleophilic centre is splayed inward; the carbonyl C is displaced from the plane of its three bonded atoms towards the nucleophile. This distortion pattern differs from that found in other 1,8-disubstituted naphthalenes and is interpreted as an expression of incipient nucleophilic addition to a carbonyl group. The crystal structure of **2b** contains an ordered arrangement of equal numbers of amino acid and zwitterionic molecules.

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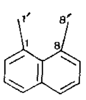
[1]) Based in part on the Doctoral Dissertation of *W. B. Schweizer,* ETH Zürich, Dissertation No. 5948.

[2]) Present address: Dyson Perrin Laboratory, South Parks Road, Oxford, England.

[3]) Present address: Department of Chemistry, Technion, Haifa, Israel.

Introduction. - Substituents in the 1- and 8-positions of naphthalene are forced into close contact - closer, in general, than the sums of their non-bonded *(van der Waals)* radii. Unusually strong interactions between such substituents are therefore to be expected. These could be manifested, for example, by distortion of the naphthalene skeleton and its exocyclic bonds, as well as by unusual chemical and spectroscopic properties. Most 1,8-disubstituted naphthalenes that have been studied by X-ray analysis show a distortion pattern consistent with a repulsion between the substituents. The exocyclic bonds are splayed outwards (**1**) and the substituents are displaced to opposite sides of the naphthalene plane to make the 1'···8' distance longer than it would be for an idealized naphthalene skeleton with 120° bond angles (*ca.* 2.45 Å). For example, d(C···C)=2.93 Å in 1,8-dimethylnaphthalene [1] and 3-bromo-1,8-dimethylnaphthalene [2], d(C···C) =2.86 Å in 1,8-di(prop-1-ynyl)naphthalene [3], and d(N···N)=2.79 Å in 1,8-bis(dimethylamino)naphthalene [4]. In 1,3,6,8-tetra(*t*-butyl)naphthalene, the most extreme example that has been studied so far [5], the distance between the *t*-butyl carbon atoms bonded to the *peri* positions is 3.86 Å.



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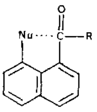

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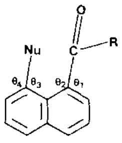

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	Nu	R
(a)	$N(CH_3)_2$	CH_3
(b)	$N(CH_3)_2$	OH
(c)	$N(CH_3)_2$	OCH_3
(d)	OCH_3	CH_3
(e)	OCH_3	OH
(f)	OCH_3	$N(CH_3)_2$
(g)	OH	$N(CH_3)_2$

By introducing nucleophilic and electrophilic centres at the 1- and 8-positions of naphthalene, we may hope to find other distortion patterns more characteristic of attraction between the substituents. A previous survey [6] of molecules containing amino and carbonyl groups has indicated that close approach between these groups tends to occur with a Nu···C=O angle of 100-110° and is accompanied by pyramidalization of the carbonyl carbon atom, *i.e.* displacement of this atom from the plane of its bonded neighbours towards the nucleophile. From this it was inferred that in nucleophilic addition to carbonyl the preferred approach direction of the nucleophile is not perpendicular to the C=O bond but makes an obtuse angle with it. However, it was difficult to exclude the possibility that the obtuse Nu···C=O angles found in the survey might be imposed by geometric constraints in the molecules examined or by other factors that have nothing to do with the nucleophilic addition process.

In a molecule of type **2** with 'natural' bond angles the Nu···C=O angle would be approximately 90°; for the typical distortion pattern **1**, the angle would be even less. Molecules of type **2** thus provide a way of testing the obtuse approach angle proposal. If the preferred Nu···C=O angle were larger than 90°, these molecules might show a different distortion pattern to **1**, one which produces an Nu···C=O angle somewhere between 90° and the preferred angle.

In what follows, we describe results of crystal structure analyses of seven *peri*-disubstituted naphthalene derivatives of type **2** (**2a**-**2g**). Details of the individual analyses are given later in the paper.

Discussion. - The exocyclic bonds of all seven molecules show a common distortion pattern **3**; the bond to the electrophilic carbon substituent is splayed outward, the bond to the nucleophile inward, *i.e.* toward the carbonyl group, by approximately the same amount. The angles between exocyclic and ring bonds (see formula **3**) are given in *Table 1* along with other relevant structural parameters. In addition to the in-plane distortion, the substituents are displaced to opposite sides of the mean plane through the naphthalene skeleton, except in **2f** where the displacements are smallest anyway. Although the amounts of the individual distortions vary from one molecule to another, the Nu···C distance remains nearly constant (2.56–2.62 Å) throughout the series, only slightly larger than the C(1)···C(8) distance (2.49–2.53 Å) and markedly shorter than in symmetrically 1,8-disubstituted naphthalenes.

It seems difficult to interpret the distortion pattern **3** in terms other than that of an attraction between the substituents. In all seven molecules the mean plane of the carbonyl group and its directly bonded neighbours is nearly perpendicular to the mean naphthalene plane. The outward bending of the exocyclic bond to the carbonyl carbon atom is evidently needed to produce a more favourable Nu···C=O angle (*i.e.* one greater than 90°). However, this distortion alone would lead to an increase in the Nu···C distance, and the inward bending of the other exocyclic bond counteracts this. Although N···C=O distances observed in aminoketones cover the whole range from non-bonded contact (~ 3.2 Å) to bonding distance (~ 1.50 Å) [6], O···C=O distances show a distinct gap between about 1.50 Å and 2.6 Å [7]. Indeed, the O···C=O distances observed in these naphthalene derivatives are among the shortest that have been found outside authentic O–C bonds[4]).

Evidence for an attractive interaction between the nucleophilic and electrophilic centres is also provided by the small but significant pyramidalization of the carbonyl carbon atom that is observed in all seven molecules (*Table 2*, for explanation of symbols see *Fig. 1*).

Although the Nu···C distance stays roughly constant, the displacement Δ_C of the carbonyl carbon atom from the plane of its three bonded atoms is clearly larger

Table 1. *Distortion of exocyclic bonds in molecules of type* **2**. The angles θ_1, θ_2, θ_3 and θ_4 are defined in formula **3**; δ(Nu) and δ(C) are the displacements of the nucleophilic atom and of the electrophilic carbon atom from the mean plane of the naphthalene skeleton

	Nu	R	θ_1	θ_2	θ_3	θ_4	δ(Nu)	δ(C)	d(C···Nu)	d(1-8)
2a	$N(CH_3)_2$	CH_3	117.2°	123.2°	116.6°	123.4°	0.10 Å	−0.11 Å	2.56 Å	2.49 Å
2b	$N(CH_3)_2$	OH	116.3	123.9	117.4	123.0	0.17	−0.15	2.61	2.49
2c	$N(CH_3)_2$	OCH_3	118.5	121.6	117.4	123.6	0.29	−0.24	2.59	2.51
2d	OCH_3	CH_3	115.3	125.5	115.9	124.4	0.08	−0.12	2.61	2.50
2e	OCH_3	OH	115.8	123.4	113.2	124.7	0.04	−0.12	2.56	2.51
2f	OCH_3	$N(CH_3)_2$	115.1	124.0	114.4	122.7	0.03	0.05	2.60	2.53
2g	OH	$N(CH_3)_2$	116.2	123.6	116.5	122.7	0.09	−0.23	2.62	2.50

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[4]) Apart from the examples in *Table 1*, the shortest O···C distances known to us involve interaction between an O atom of an aromatic nitro group and carbonyl C: 2.58 Å in 3-chloro-2′-nitrochalcone [8], 2.59 Å in 1,3-dimethyl-3-(2′-nitrophenyl)-pyrrolidine-2,5-dione [9] and 2.60 Å in the corresponding 1-monomethyl derivative [9].

Table 2. *Geometric relationships between nucleophilic and electrophilic substituents in molecules of type* **2** (For explanation of the symbols see *Fig. 1*)

	Nu	R	$d(\mathrm{Nu}\cdots\mathrm{C})$	α	β	γ	δ	Δ_C	Δ_N
2a	$N(CH_3)_2$	CH_3	2.56 Å	104.4	92.6	83.7	93.7	0.088 Å	0.402 Å
2b	$N(CH_3)_2$	OH	2.61	102.2	92.5	83.0	92.3	0.061	0.386
2c	$N(CH_3)_2$	OCH_3	2.59	98.6	94.4	84.3	91.5	0.062	0.397
2d	OCH_3	CH_3	2.61	107.6	87.7	80.0	96.2	0.044	-
2e	OCH_3	OH	2.56	93.7	97.4	80.9	97.7	0.02	-
2f	OCH_3	$N(CH_3)_2$	2.60	103.3	90.0	80.8	96.4	0.039	(0.113)
2g	OH	$N(CH_3)_2$	2.62	97.0	97.8	81.2	94.2	0.051	(0.070)

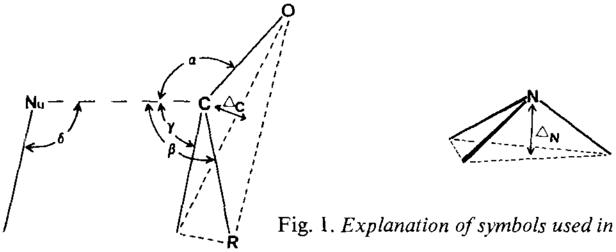

Fig. 1. *Explanation of symbols used in* Table 2

(0.06-0.09 Å) for Nu = $N(CH_3)_2$ than for Nu = OCH_3 or OH (0.02-0.05 Å). This may be interpreted as a structural expression of the better nucleophilicity of amino nitrogen as compared with ether or phenolic oxygen.

Similarly, the variation of Δ_C with different R but constant nucleophile might be expected to parallel the relative electrophilicity of the carbonyl carbon atom (CO–R > COOH ~ COOR > $CONR_2$). As far as our limited data are concerned, this holds for the ketones, acids, and esters, but the amides do not fit the pattern, since the hydroxy amide **2g** has the largest Δ_C in the O···C=O series. This minor anomaly is probably due to special features of the molecular packing. The intermolecular hydrogen bonding between the hydroxyl group of one molecule and the carbonyl oxygen atom of its neighbour can be regarded as representing an incipient stage of a proton transfer process ($O{-}H\cdots O{=}C \rightarrow O^-\cdots H{-}O^+{=}C$). As a result of this hydrogen bonding, the donor oxygen atom becomes slightly more nucleophilic and the carbonyl carbon atom becomes slightly more electrophilic than in the isolated molecule. In **2f**, where the hydrogen bond is absent, Δ_C is smaller than in **2g**.

Table 2 shows that the Nu···C=O angle α is always larger than 90°. However, in spite of the geometric constraints imposed by the naphthalene skeleton there is a moderate variation in this angle (94–108°) and also in the Nu···C–R angle β (88–98°). This is achieved mainly by rotation of the carbonyl plane around the exocyclic C(8)–C bond. The difference between the angles α and β tells us something about the approach direction of the nucleophile with respect to the R–C=O group *(Fig. 2)*. For $\alpha \gg \beta$, as in the ketones **2a** and **2d**, the approach is roughly along the extension of the O=C direction; for $\alpha \sim \beta$, as in the carboxylic acid derivatives **2c** and **2e**, with electronegative R groups, the approach is more nearly along the bisector of the R–C=O angle. The disparity in approach direction between the two carboxylic acids **2b** and **2e** is noteworthy. In **2b**, α is 10° greater than β, and the C=O bond is clearly differentiated from the C–OH bond by a 0.1 Å

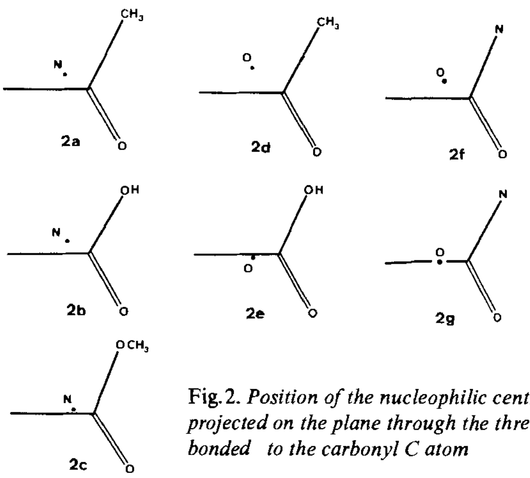

Fig. 2. *Position of the nucleophilic centre* (N or O) *projected on the plane through the three atoms directly bonded to the carbonyl C atom*

difference in bond length (1.215 Å *vs.* 1.326 Å). In **2e**, $\alpha \sim \beta$ and the two C–O bond lengths differ only by 0.02 Å (1.228 Å *vs.* 1.253 Å). The likely origin of this disparity lies in the different hydrogen bonding patterns found in the respective crystal structures. Similarly, the disparity in approach direction between the methoxy-amide **2f** and the hydroxy-amide **2g** can also be discussed in terms of incipient protonation of the amide group in the latter (*cf.* the discussion of the anomalously large Δ_C of **2g**).

On the whole, the pattern of approach directions shown in *Figure 2* is reasonably consistent with expectations based on several simple models of chemical bonding and reactivity, including the vector analysis rules recently proposed by *Baldwin* [10]. However, the variability in approach direction associated with minor differences in structure and crystal packing (analogous to solvent effects) points to a certain latitude in the interpretation of these models and calls for caution in making predictions based on them.

The Δ_N values listed in *Table 2* show that the amino nitrogen atom in **2a**, **2b**, **2c** is strongly pyramidal, *i.e.* it has more the character of an aliphatic amine than of an

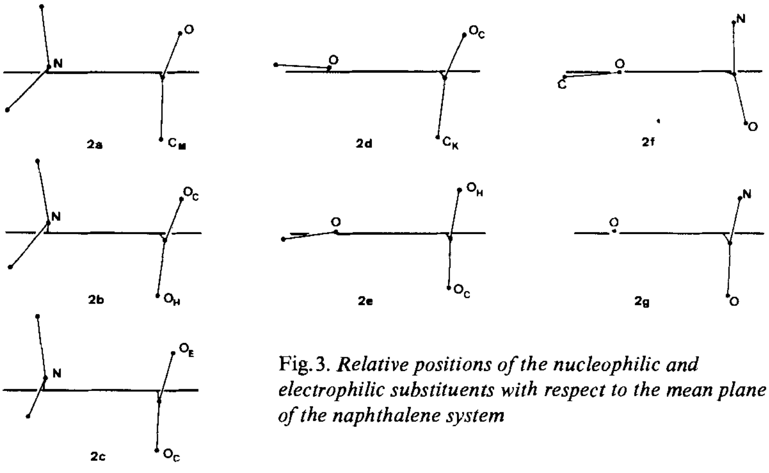

Fig. 3. *Relative positions of the nucleophilic and electrophilic substituents with respect to the mean plane of the naphthalene system*

aromatic one. As may be inferred by inspection of *Figure 3*, the nitrogen lone-pair orbital axis in these molecules is forced to lie nearly in the plane of the naphthalene system, so that conjugation with the aromatic π-orbitals is not possible.

The Δ_N values of the amide nitrogen atom of **2f** and **2g** are 0.113 Å and 0.070 Å, respectively, and the displacements are in the opposite sense to those of the carbonyl carbon atoms, *i.e.* the carbon atom displacement is towards the nucleophilic oxygen atom, and the nitrogen atom displacement is away from it *(Fig. 4)*. This result fits nicely with the stereoelectronic theory recently proposed by *Deslongchamps* [11] for the breakdown of the tetrahedral intermediate formed during the hydrolysis of esters and *N*-disubstituted imidates. In this theory, cleavage of a specific C–O or C–N bond of the tetrahedral adduct is allowed only if the bond in question is antiperiplanar to lone-pair orbitals on the other two heteroatoms. Microscopic reversibility would then imply that in the *formation* of the tetrahedral intermediate, the developing lone-pair orbitals on the heteroatoms must be antiperiplanar to the developing bond. It can be seen from *Figure 4* that this condition is approximately fulfilled as far as the amide nitrogen atom is concerned[5]).

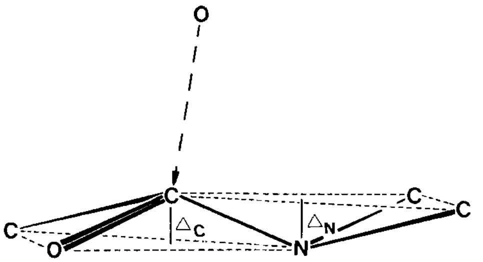

Fig. 4. *Schematic representation of the type of deformation observed for the* N,N*-dimethyl amide group in molecules* **2f** *and* **2g**

The difference between Δ_N for **2f** and **2g** (like the difference between the Δ_C values and the disparity between nucleophile approach directions) can be attributed to features of the molecular packing. The incipient protonation of the amide group of **2g** leads to an increase in the double-bond character of the C-NMe$_2$ bond, and hence to an increased resistance to out-of-plane bending at the nitrogen atom. The bond lengths and angles in the amide groups of **2f** and **2g** also show small differences that are consistent with patterns observed for protonated and nonprotonated amides [13].

The orientation of the substituents with respect to the naphthalene nucleus is very similar throughout the series *(Fig. 3)*. In all cases the mean plane of the electrophilic COR-substituent is nearly perpendicular to the naphthalene plane. When a $N(CH_3)_2$ substituent is present it is oriented such that its lone-pair direction points roughly towards the carbonyl C atom of the electrophilic substituent. When the nucleophile is a methoxy group the O–C bond lies approximately in the naphthalene plane; for this group it is thus the *sp*^{2} lone pair of the oxygen atom that points towards the electrophilic C atom – the *p* lone pair is then oriented so as to conjugate with the π-electrons of the naphthalene nucleus.

The geometry of the naphthalene nucleus is also very similar throughout the series; deviations of individual bond lengths and bond angles from their mean

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[5]) For possible implications in enzyme-catalyzed hydrolysis of peptides see [12].

values do not much exceed 0.01 Å and 1° respectively, except for the internal bond angles at C(1) and C(2), which show a just detectable dependence on the nature of the nucleophilic group at C(1). When this is $N(CH_3)_2$, the C(1) angle tends to be slightly smaller than 120°, the C(2) angle slightly larger; when the substituent is OCH_3, these relationships are reversed. Analogous effects of substituents on the bond angles in benzene derivatives have been noted [14].

Despite the out-of-plane bending of the exocyclic bonds *(Table 1)*, the naphthalene skeleton is virtually planar in the methoxy and hydroxy derivatives **2d**-**2g**, where displacements of individual carbon atoms from the mean plane do not exceed 0.02 Å. In the dimethylamino ketone **2a**, the displacements are not much larger (up to 0.03 Å), but in the two other dimethylamino derivatives **2b** and **2c**, where displacements of the substituents from the naphthalene plane are largest, the out-of-plane deformation of the skeleton becomes considerable. For these molecules the displacements of individual atoms are (in units of 10^{-2} Å):

	1	2	3	4	5	6	7	8	9	10	N	C
2b	5	1	−5	−2	2	1	−3	−4	1	2	17	−15
2c	9	1	−8	−3	6	3	−6	−6	2	3	29	−24

The out-of-plane deformation of the naphthalene nucleus is thus seen to be mainly along the symmetry coordinate

$$S(A_u) = \Delta z_1 + \Delta z_2 - \Delta z_3 - \Delta z_4 + \Delta z_5 + \Delta z_6 - \Delta z_7 - \Delta z_8$$

that preserves D_2 symmetry of the skeleton.

Crystal Structure Analyses. - Crystallographic data and details of intensity measurements are given in *Table 3* for all seven compounds; **2a**, **2b**, **2d** and **2e** were measured with a Y 290 *(Hilger and Watts)* diffractometer, **2c**, **2f**, and **2g** with a CAD-4 (ENRAF Nonius). The crystal structures were solved with the help of direct methods (MULTAN programme [15]) and refined by full-matrix least-squares analysis with anisotropic thermal parameters for C, N, and O atoms, isotropic for H atoms. For structure **2b**, with two molecules in the asymmetric unit, each molecule was treated as a separate block. Final positional and vibrational parameters for compounds **2a**-**2g** are tabulated in the descriptions of the individual analyses.

Thermal Motion Analyses. - The bond lengths and bond angles shown in the various *Figures* are uncorrected for thermal motion effects. Analysis of the vibrational tensors shows that the molecules do not vibrate as rigid bodies but are subject to internal motions of considerable amplitude in some cases. As a test of molecular rigidity we have used the criterion that the mean-square vibrational amplitudes of any pair of atoms in a rigid body should be equal in the direction along the interatomic vector [16]. This criterion is a generalization of *Hirshfeld*'s rigid-bond postulate [17], which states that if $Z^2_{A,B}$ is the mean-square vibrational amplitude of atom A in the direction of a bond AB, then $\Delta_{AB} = Z^2_{A,B} - Z^2_{B,A} \sim 0$ for any pair of bonded atoms. In a rigid body all pairs of atoms can be regarded as being connected

Table 3. *Crystallographic data and experimental details*

	2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**
Formula	$C_{14}H_{15}NO$	$C_{13}H_{13}NO_2$	$C_{14}H_{15}NO_2$	$C_{13}H_{12}O_2$	$C_{12}H_{10}O_3$	$C_{14}H_{15}NO_2$	$C_{13}H_{13}NO_2$
Space Group	$P2_1/c$	$P2_1/n$	$P2_12_12_1$	Pc	$C2/c$	$Pbca$	$P2_12_12_1$
a(Å)	8.470	8.499	7.630	8.561	29.712	15.174	9.019
b(Å)	10.340	12.485	10.854	9.047	6.940	11.771	15.815
c(Å)	14.348	21.518	14.962	7.378	9.791	14.156	7.998
β(deg)	109.15	90.90	90	110.53	90.78	90	90
Z	4	8	4	2	8	8	4
D_x(g cm^{-3})	1.229	1.253	1.193	1.242	1.331	1.208	1.252
Reflections measured	2319	3456	1247	851	1797	2183	1454
Significant[a])	1937	2181	1054	560	1191	649	1083
Weighting[b])	$p=10$	$\sigma^{-1}(F_o)$	$p=6$	$\sigma^{-1}(F_o)$	$\sigma^{-1}(F_o)$	$p=5$	$p=5$
R	0.047	0.056	0.038	0.053	0.078	0.095	0.029

[a]) Reflections were regarded as significant if $I > 3\sigma_I$.

[b]) The value of p refers to the use of a modified weighting system $\omega = \sigma^{-1}(F_o)\exp(p\sin^2\theta/\lambda^2)$.

Table 4. *Values of* $\Delta_{AB} = Z^2_{A,B} - Z^2_{B,A}$ *for all atom-pairs (bonds bold-face) for molecule* **2e** (calculated from positional coordinates and vibrational parameters of *Table 9*). The quantity $Z^2_{A,B}$ is the mean-square vibrational amplitude of atom A along the direction from A to B. All values in units of 10^{-4} Å^2

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	O_M	C_M	C_C	O_C	O_H
C(1)	-	+**68**	−42	−100	−15	+43	+118	+114	+**29**	−25	−**28**	−112	+93	−528	−230
C(2)		-	−**92**	+63	+9	+23	+94	+22	+19	+75	+3	−207	+20	−673	−308
C(3)			-	+**103**	−75	−74	+41	−65	−44	−19	+71	−108	−27	−481	−241
C(4)				-	−99	−55	+130	+38	+68	+**19**	+75	−122	+48	−181	−58
C(5)					-	+**13**	+44	−7	−33	+**67**	+48	−21	−30	−16	−26
C(6)						-	−**90**	+15	−26	+57	+38	−8	−17	−64	−49
C(7)							-	+**87**	−73	−111	+83	+40	+127	−43	+123
C(8)								-	+**18**	−16	0	−45	−**15**	+25	−17
C(9)									-	−**11**	+79	+16	−19	−195	−112
C(10)										-	+56	−55	+15	−64	−43
O_M											-	−77	+47	−565	−331
C_M												-	+127	+909	−155
C_C													-	−**46**	+**49**
O_C														-	+53
O_H															-

by virtual bonds, so the value of $\langle \Delta^2_{\mathrm{AB}} \rangle^{1/2}$ averaged over nonbonded pairs should be approximately the same as $\langle \Delta^2_{\mathrm{AB}} \rangle^{1/2}$ averaged over bonded pairs. This relationship among the mean-square amplitudes is a necessary condition for the validity of the rigid-body model, but it is not sufficient because any vibrational component perpendicular to the AB direction leaves $\Delta_{\mathrm{AB}} \sim 0$. For example, the out-of-plane vibrations of a planar skeleton (like naphthalene) may be large enough to invalidate the rigid-body model, but they make no contribution to Δ_{AB} for AB pairs within the skeleton.

Subject to this indeterminacy, the rigid-body test is obeyed quite well for the naphthalene skeletons and for the two atoms directly bonded to C(1) and C(8) in all the examples tested; that is, the r.m.s. value of Δ_{AB} averaged over all nonbonded pairs within these fragments is not significantly greater than the value obtained by averaging over bonds. However, the r.m.s. value averaged over bonds is usually larger (by a factor of 1.5–2) than the value expected from the estimated standard deviations $\sigma(U_{ij})$ of the experimental U_{ij} values. This is not too surprising, because U_{ij} will always be contaminated by various kinds of systematic errors, whereas $\sigma(U_{ij})$ only includes the effect of random errors in the experimental data. For this reason, we tend to regard the value of $\langle \Delta^2_{\mathrm{AB}} \rangle^{1/2}_{bonds}$ as a more realistic estimate of the errors to be expected in the U_{ij} values than $\sigma(U_{ij})$.

Values of Δ_{AB} for vectors between atoms of the naphthalene skeleton and those of the substituents are often many times larger than $\langle \Delta^2_{\mathrm{AB}} \rangle^{1/2}_{bonds}$, suggesting that the substituent groups are carrying out large amplitude motions relative to the naphthalene skeleton.

As an example, Δ_{AB} values for the methoxy carboxylic acid **2e** are given in *Table 4*. The r.m.s. value for the 16 bonds is 0.0059 Å^2, with a maximum Δ of 0.0103 Å^2. Very similar values are obtained for the 53 nonbonded pairs in the fragment consisting of the naphthalene skeleton and its directly bonded substituents $\mathrm{O_M}$ and $\mathrm{C_C}$ (r.m.s. value, 0.0061 Å^2; maximum value, 0.0130 Å^2). In contrast, some of the Δ values for nonbonded pairs involving the methyl carbon $\mathrm{C_M}$ and the carboxyl oxygen atoms $\mathrm{O_C}$ and $\mathrm{O_H}$ are many times larger, indicating that these atoms undergo appreciable motions relative to the naphthalene skeleton. Under these circumstances any attempt to reproduce the observed U_{ij} values by calculations based on a rigid-body model can hardly be very successful. Indeed, analysis of the observed U_{ij} values in terms of rigid-body vibrations [18] leads to poor agreement: $R(U_{ij}) = [\Sigma(\Delta U_{ij})^2/\Sigma(U_{ij}^2)]^{1/2} = 0.213$, $M(U_{ij}) = \langle(\Delta U_{ij})^2\rangle^{1/2} = 0.0098$ Å^2, $S(U_{ij}) = \langle \sigma^2(U_{ij}) \rangle^{1/2} = 0.0025$ Å^2 (a more realistic value might be $2^{-1/2}\langle \Delta^2_{\mathrm{AB}} \rangle_{bonds} \sim 0.0042$ Å^2).

Much improved agreement is obtained when the analysis is repeated with allowance for internal molecular motions [19]. The most important kinds of internal motion can be inferred from inspection of the U_{ij} values (conveniently transformed to a coordinate system based on principal inertial axes of the naphthalene skeleton) or of the thermal ellipsoid pattern. They are: (*a*) torsional vibration of the carboxyl group around the C(8)–C-bond; (*b*) out-of-plane bending vibration of the methoxy group; (*c*) C(1)–O–$\mathrm{C_M}$ bond-angle bending vibration. With inclusion of these three types of internal motion we obtain: $R(U_{ij}) = 0.104$, $M(U_{ij}) = 0.0048$ Å^2; the agreement indices are now about as good as can be expected. The corresponding r.m.s. amplitudes for the three kinds of internal vibration (and their standard deviations) are: (1) 14.0° (0.7°); (2) 14.6° (0.7°); (3) 6.8° (1.5°).

Similar results are obtained for the other six analyses (some details are given in the following descriptions of the individual crystal structures). In general, the molecules do not behave as rigid bodies, and the relative motion of substituent groupings can be approximated as a torsional vibration about the exocyclic bond in question.

Because of the failure of the rigid-body model to account for the vibrational parameters obtained in these analyses, thermal motion corrections based on the assumption of rigid-body motion cannot be considered trustworthy. A rough and ready allowance for thermal motion errors can be made by adding about 0.005 Å to the uncorrected bond lengths shown in the *Figures.*

Table 5. *Compound* **2a**: *positional and vibrational parameters* (standard deviations in parentheses). The temperature factor expression is $\exp[-2\pi^2(U_{11}h^2a^{*2}+\cdots 2\,U_{12}hka^*b^*\cdots)]$ for non-hydrogen atoms, $\exp(-B\sin^2\theta/\lambda^2)$ for hydrogen atoms

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	1.0707 (3)	.5872 (2)	.1967 (2)	.0458	.0411	.0414	-.0016	.0165	-.0032
C2	.9964 (3)	.5168 (2)	.2520 (2)	.0580	.0535	.0496	-.0006	.0207	.0083
C3	.8268 (3)	.5345 (2)	.2409 (2)	.0655	.0603	.0538	-.0126	.0334	-.0000
C4	.7341 (3)	.6230 (2)	.1762 (2)	.0469	.0570	.0592	-.0055	.0264	-.0073
C5	.7096 (3)	.7880 (2)	.0470 (2)	.0395	.0555	.0585	.0006	.0121	-.0027
C6	.7800 (3)	.8573 (2)	-.0092 (2)	.0534	.0568	.0595	.0036	.0052	.0101
C7	.9475 (3)	.8362 (2)	-.0011 (2)	.0519	.0587	.0495	-.0052	.0157	.0080
C8	1.0446 (3)	.7486 (2)	.0639 (2)	.0427	.0390	.0353	-.0043	.0113	-.0024
C9	.9750 (2)	.6767 (2)	.1255 (1)	.0403	.0363	.0380	-.0033	.0117	-.0052
C10	.8049 (3)	.6964 (2)	.1160 (2)	.0422	.0417	.0422	-.0053	.0139	-.0078
C(M)	1.2471 (3)	.6224 (2)	-.0005 (2)	.0698	.0847	.0673	-.0029	.0296	-.0286
C(N1)	1.3056 (4)	.4437 (3)	.2095 (2)	.0952	.0628	.1632	.0323	.0763	.0367
C(N2)	1.3480 (3)	.6534 (3)	.2902 (2)	.0554	.1371	.0517	-.0165	.0070	-.0068
C(O)	1.2200 (3)	.7300 (2)	.0630 (2)	.0486	.0530	.0455	-.0043	.0178	-.0003
N	1.2435 (2)	.5766 (2)	.2069 (1)	.0450	.0463	.0598	.0056	.0177	.0059
O	1.3268 (2)	.8116 (1)	.0980 (1)	.0530	.0579	.0901	-.0162	.0271	-.0076

	x	y	z	B(Å^2)
H2	1.061 (3)	.455 (2)	.303 (2)	5.4
H3	.777 (3)	.484 (2)	.280 (2)	4.6
H4	.613 (2)	.638 (2)	.165 (1)	3.3
H5	.585 (3)	.800 (2)	.042 (1)	3.8
H6	.713 (3)	.924 (2)	-.058 (2)	5.9
H7	1.000 (3)	.882 (2)	-.048 (2)	5.4
H1(CM)	1.369 (4)	.602 (3)	.015 (2)	9.8
H2(CM)	1.186 (4)	.547 (3)	.003 (2)	9.2
H3(CM)	1.195 (4)	.654 (3)	-.069 (2)	10.7
H1(CN1)	1.223 (4)	.394 (3)	.150 (2)	9.6
H2(CN1)	1.304 (5)	.401 (4)	.274 (3)	14.9
H3(CN1)	1.417 (4)	.452 (3)	.202 (2)	11.5
H1(CN2)	1.342 (3)	.614 (3)	.357 (2)	9.4
H2(CN2)	1.298 (4)	.740 (3)	.287 (2)	11.8
H3(CN2)	1.466 (4)	.653 (3)	.290 (2)	10.8

Crystal Structure of 8-(*N*, *N*-Dimethylamino)-1-naphthyl Methyl Ketone (2a). – Atomic parameters are given in *Table 5.* The only atoms that have vibrational tensor components (U_{ij}) greater than 0.1 Å^2 are the two carbon atoms of the dimethylamino group. The shapes of the vibrational ellipsoids *(Fig. 5)*[6]) give the impression that this group makes a torsional vibration about the exocyclic C–N bond. Detailed analysis of the vibrational tensors in terms of rigid-body motion [18]

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[6]) In the stereoviews of molecules **2a–2g** *(Fig. 5, 8, 9, 12, 15, 18, 22,* and *25)* vibration ellipsoids are drawn at the 50% probability level using computer program ORTEP [20]. Packing diagrams *(Fig. 7, 11, 14, 17, 20, 23,* and *26)* were drawn either with the ORTEP or with the PLUTO [21] programs.

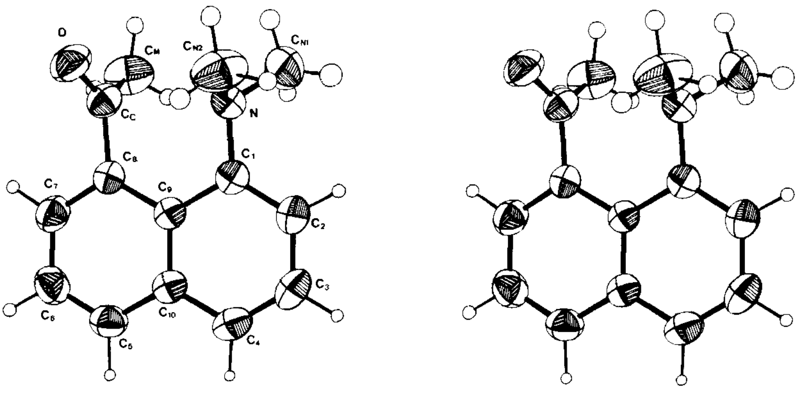


Fig. 5. *Stereoview of molecule* **2a**

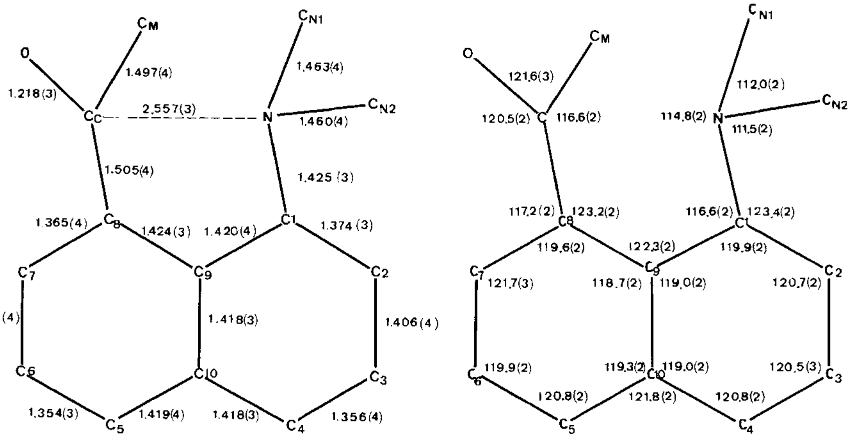


Fig. 6. *Bond lengths and angles in molecule* **2a**

with allowance for torsional vibrations about the exocyclic bonds [19] leads to r.m.s. torsional amplitudes of 9.1° ($\sigma = 0.7°$) for the $N(CH_3)_2$ group and of 8.6° ($\sigma = 0.7°$) for the $COCH_3$ group. This description of the internal molecular motion improves the agreement between observed and calculated U_{ij} values compared with the rigid-body model ($R(U_{ij}) = 0.163$, $M(U_{ij}) = 0.0060$ Å^2) but it still leaves large discrepancies [$R(U_{ij}) = 0.119$, $M(U_{ij}) = 0.0043$ Å^2].

Bond lengths and angles, uncorrected for thermal motion, are given in *Figure 6*. Thermal motion corrections amount to +0.005-0.007 Å for all bonds except those involving the methyl C-atoms, where they are slightly more (+0.009 Å). Corrections to bond angles are negligibly small.

The molecular packing is shown in *Figure 7*.

Crystal Structure of 8-(*N,N*-Dimethylamino)-naphthalene-1-carboxylic Acid (2b). - Crystals of **2b** have the remarkable property that they are built from two kinds of molecules, those of the amino acid itself and those of the zwitterion, in an ordered arrangement.

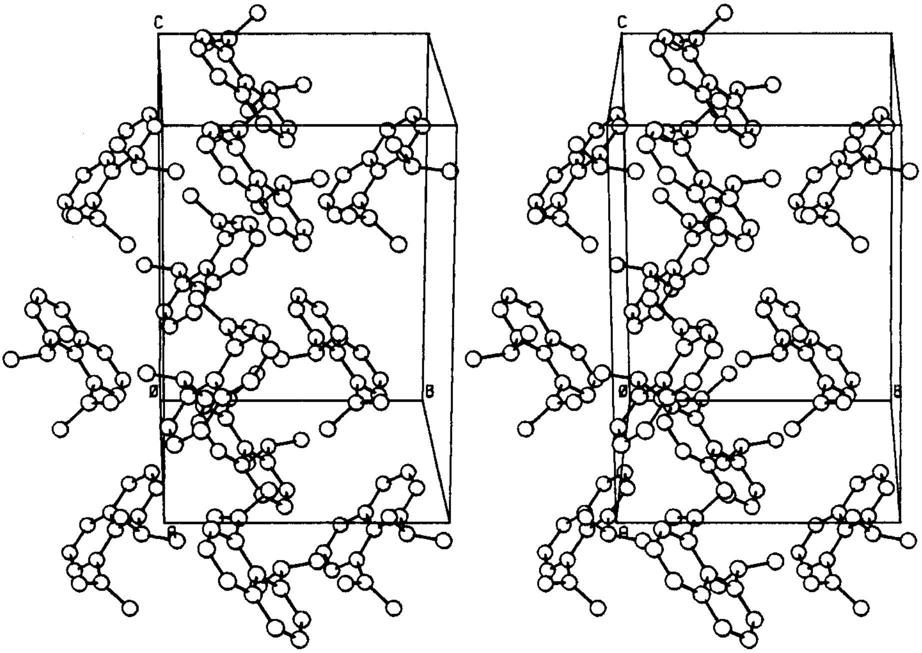


Fig. 7. *Crystal packing of compound* **2a**

The co-existence of an amino acid and its zwitterion in one and the same crystal structure is unusual but it is not unique; it also occurs in anthranilic acid [22]. In our case, the two tautomers are easily distinguished by differences in atomic arrangement. The amino acid shows the same characteristic distortion pattern of the exocyclic bonds as found in the other molecules of type **2**; the N···C distance is 2.61 Å, and the mean plane of the carboxyl group is nearly perpendicular to the naphthalene plane, as can be seen from *Figure 8.* In the zwitterion *(Fig. 9),* the carboxylate group lies nearly in the naphthalene plane and both exocyclic bonds are splayed outwards to give an N···C distance of 3.14 Å. The acid proton is bonded to the N atom (N–H, 1.14(3) Å), but it is also engaged in an unusually short intramolecular hydrogen bond to one of the carboxylate O atoms (H···O, 1.32(3) Å, N···O, 2.45 Å). The other carboxylate O-atom forms an intermolecular hydrogen bond with the acid proton of an amino acid molecule (OH···O, 2.60 Å).

There are also marked differences in bond lengths and angles between the two molecules (see *Fig. 10*). In the zwitterion the N–C distances are longer (change from three- to four-coordinated N) and the bond angles C(1)–C(9)–C(8) and C(9)–C(8)–C_C are larger (relief of steric congestion) than in the amino acid. Also the exocyclic bond to the carboxylate anion (in the naphthalene plane) is slightly longer than the corresponding bond to the carboxyl group (perpendicular to the naphthalene plane).

As a result of the intermolecular hydrogen bonding between carboxyl and carboxylate groups, amino acid and zwitterionic molecules pair off into dimers, as illustrated in the molecular packing diagram *(Fig. 11).*

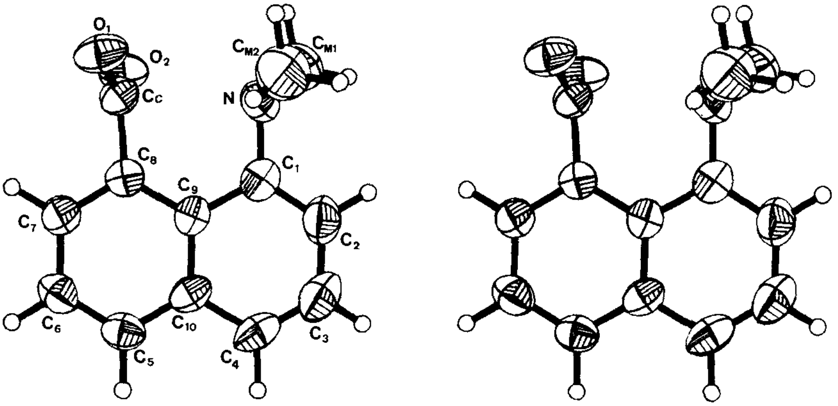


Fig. 8. *Stereoview of molecule* **2b** (amino acid isomer)

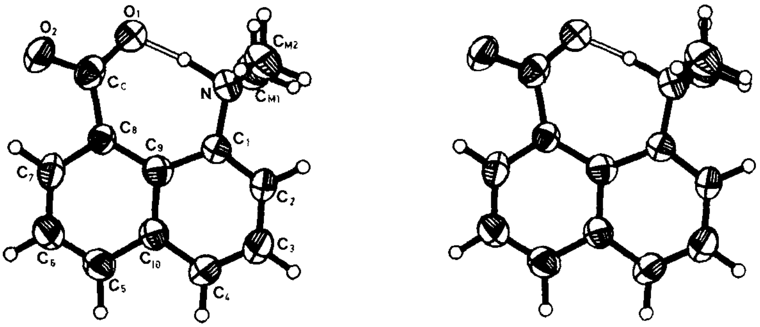


Fig. 9. *Stereoview of molecule* **2b** (zwitterionic form)

Atomic parameters for both molecules in the asymmetric unit are listed in *Table 6*. As in the ketone **2a**, the only atoms in the amino acid molecule with U_{ij} values greater than 0.1 Å^2 are the two methyl C-atoms of the dimethylamino group. In the zwitterion the vibrational parameters of these atoms are smaller than in the amino acid, but several of the ring atoms, and one of the carboxylate O-atoms, have $U_{ij} > 0.1$ Å^2. A detailed thermal motion analysis was not carried out for this crystal.

Crystal Structure of Methyl 8-(*N*,*N*-Dimethylamino)naphthalene-1-carboxylate (2c). - As mentioned in the Discussion, this molecule shows the largest out-of-plane bending of the exocyclic bonds and also the largest out-of-plane deformation of the naphthalene skeleton.

Atomic parameters are listed in *Table 7*. Although the mean-square vibrational amplitudes of the atoms of the naphthalene skeleton are generally somewhat higher than in the aminoketone **2a**, those of the substituents are somewhat lower. Detailed analysis of the vibrational tensors along the same lines as for compound **2a** leads to r.m.s. torsional vibrations of 6.9° ($\sigma = 0.8°$) for the $N(CH_3)_2$ group and of 4.8°

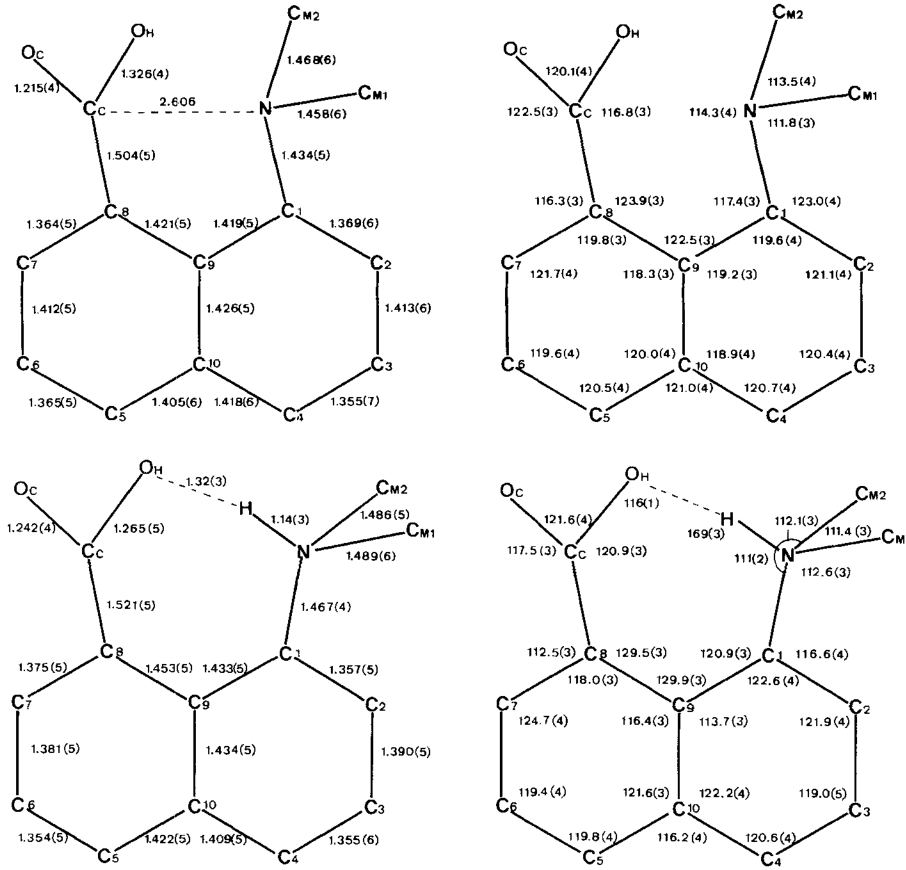


Fig. 10. *Bond lengths and bond angles in amino acid* **2b** (above) *and zwitterion* **2b** (below)

($\sigma = 1.2°$) for the ester group. The agreement between observed and calculated U_{ij} values is about the same as that obtained for **2a** [$R(U_{ij}) = 0.100$, $M(U_{ij}) = 0.0045$ Å^2].

A stereoview of the molecule is shown in *Figure 12*, and bond lengths and angles are given in *Figure 13*. The bond lengths are subject to thermal motion corrections of about +0.005 Å.

The crystal structure *(Fig. 14)* contains well-defined stacks of molecules related by a twofold screw-axis parallel to **b**. Within a given stack, the ester group of one molecule is sandwiched between dimethylamino groups of adjacent molecules, and *vice versa.* Note that the space group of **2c** (in contrast to **2a** and **2b**) does not contain inversion centres or glide planes; all molecules within a single crystal have the same chirality sense.

Crystal Structure of 8-Methoxy-1-naphthyl Methyl Ketone (2d). - The pseudosymmetrical nature of this crystal structure led to some difficulties in the analysis. The space group is *Pc*, but the midpoint of the centrosymmetric naphthalene nucleus has a *y*-coordinate close to 0.25, so that if the substituents are neglected the

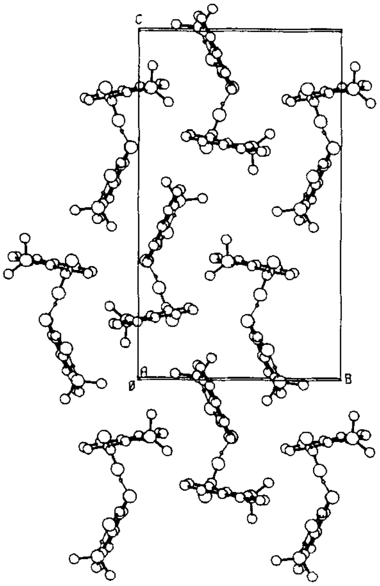


Fig. 11. *Crystal packing of compound* **2b**

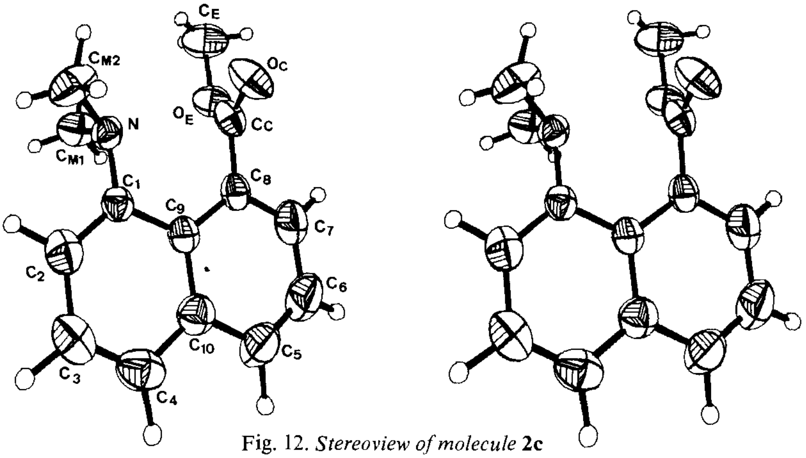


Fig. 12. *Stereoview of molecule* **2c**

molecular arrangement conforms almost exactly to the higher space group $P2_1/c$. The final atomic parameters are listed in *Table 8;* they are somewhat less accurate than in the other analyses, partly because of the pseudosymmetry and partly because of the limited amount of intensity data available (see *Table 3*). Note that for this crystal the H coordinates were calculated from the heavy-atom positions but not refined.

A stereoview of the molecule is shown in *Figure 15,* bond lengths and angles are given in *Figure 16.* The molecular packing, shown in *Figure 17,* is characterized by the pronouncedly polar layers lying in the bc plane; all layers have the same polarity sense.

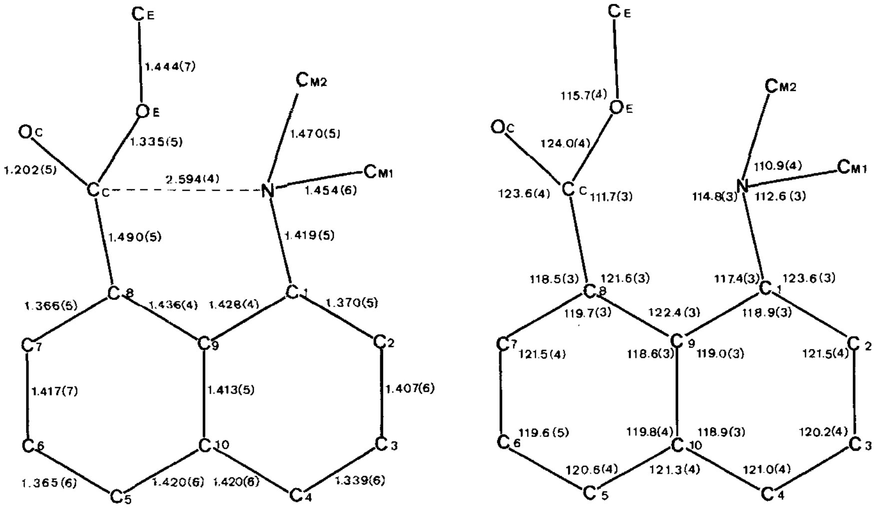


Fig. 13. *Bond lengths and angles in molecule* **2c**

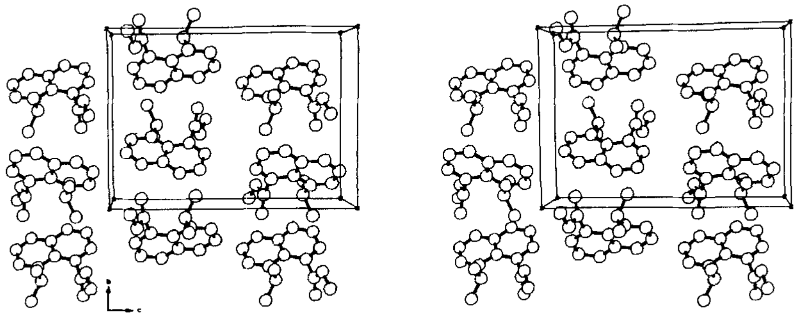


Fig. 14. *Crystal packing of compound* **2c**

Crystal Structure of 8-Methoxynaphthalene-1-carboxylic Acid (2e). - Atomic parameters are listed in *Table 9;* the vibrational parameters, especially those of the carboxyl oxygen atoms and of the methoxy carbon atom, are large ($U \sim 0.15$ Å^2). The shapes of the vibrational ellipsoids *(Fig. 18)* suggest that in addition to any rigid-body molecular motion that may be present, the substituents carry out appreciable motions relative to the naphthalene skeleton. This is confirmed by detailed analysis of the vibrational tensors (see discussion in Section on Thermal Motion Analysis).

Bond lengths and angles are shown in *Figure 19.* Note that the two C–O bonds of the carboxyl group are nearly equal in length (1.23 Å *vs.* 1.25 Å compared with 1.22 Å *vs.* 1.33 Å in the amino acid **2b**). This is probably a result of disorder. As can be seen from the packing diagram *(Fig. 20)* the molecules are associated into dimers by pairs of hydrogen bonds (OH···O = 2.69 Å) between carboxyl groups across inversion centres - the normal mode of association of carboxylic acids [23]. Apart from the acid protons, the dimers of **2e** are approximately mirror symmetric (methoxy groups lie in the plane, carboxyl groups perpendicular to it). The two

Table 6. *Compound* **2b**: *positional and vibrational parameters.* Atoms belonging to the zwitterionic molecule are marked with an additional number 1. See caption to *Table 5* for other details

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	.3170 (4)	.1764 (3)	.4970 (2)	.0421	.0640	.0461	-.0041	-.0001	-.0021
C2	.4211 (4)	.2058 (4)	.5423 (2)	.0554	.1014	.0464	-.0062	.0007	-.0198
C3	.5818 (5)	.1901 (4)	.5365 (2)	.0617	.1195	.0535	-.0146	-.0104	-.0162
C4	.6359 (4)	.1460 (4)	.4835 (2)	.0469	.1002	.0552	-.0003	-.0069	-.0063
C5	.6003 (4)	.0730 (3)	.3807 (2)	.0493	.0688	.0535	-.0005	.0074	.0038
C6	.5077 (5)	.0423 (3)	.3322 (2)	.0580	.0774	.0555	-.0049	.0149	-.0125
C7	.3465 (4)	.0498 (3)	.3370 (2)	.0650	.0568	.0414	-.0151	-.0012	-.0059
C8	.2697 (4)	.0897 (3)	.3879 (1)	.0465	.0451	.0376	-.0031	.0006	.0045
C9	.3642 (4)	.1267 (3)	.4404 (2)	.0482	.0506	.0390	-.0033	.0024	.0068
C10	.5313 (4)	.1147 (3)	.4355 (2)	.0505	.0545	.0434	-.0003	.0018	.0026
C(C)	.0920 (4)	.0898 (3)	.3789 (2)	.0581	.0616	.0423	-.0090	-.0055	.0098
C(M1)	.1188 (5)	.3157 (4)	.5161 (2)	.0786	.0680	.0841	.0167	-.0092	-.0179
C(M2)	.0897 (5)	.1366 (4)	.5616 (2)	.0680	.0953	.0640	-.0031	.0167	.0020
N	.1508 (3)	.1994 (3)	.5085 (1)	.0527	.0662	.0461	.0008	.0014	-.0088
O(C)	.0367 (3)	.0388 (2)	.3340 (1)	.0630	.0824	.0509	-.0085	-.0155	-.0049
O(H)	.0041 (3)	.1399 (3)	.4158 (1)	.0472	.1221	.0730	.0001	-.0029	-.0376
C1 1	.0836 (4)	-.0435 (3)	.1653 (2)	.0594	.0601	.0460	.0097	.0032	-.0015
C2 1	.1885 (5)	-.1243 (3)	.1553 (2)	.0822	.0605	.0753	.0079	.0011	-.0150
C3 1	.3521 (5)	-.1048 (4)	.1550 (2)	.0801	.0886	.0787	.0294	.0085	-.0124
C4 1	.4082 (5)	-.0041 (4)	.1630 (2)	.0565	.0913	.0565	.0181	.0075	-.0037
C5 1	.3619 (4)	.1864 (3)	.1836 (2)	.0521	.0680	.0531	-.0077	-.0015	.0119
C6 1	.2609 (5)	.2685 (3)	.1963 (2)	.0575	.0583	.0690	-.0129	-.0086	.0018
C7 1	.0984 (4)	.2478 (3)	.2008 (2)	.0538	.0570	.0605	.0046	-.0028	-.0011
C8 1	.0381 (4)	.1478 (3)	.1920 (1)	.0460	.0504	.0312	.0008	-.0010	.0051
C9 1	.1395 (4)	.0616 (3)	.1769 (1)	.0541	.0486	.0330	.0055	.0032	.0023
C10 1	.3041 (4)	.0822 (3)	.1738 (2)	.0467	.0680	.0378	.0081	.0075	.0068
C(C) 1	.1360 (4)	.1358 (3)	.2010 (2)	.0504	.0543	.0485	.0039	.0028	.0036
C(M1) 1	.1431 (6)	-.0652 (5)	.0992 (2)	.0936	.1222	.0940	.0083	-.0322	-.0389
C(M2) 1	.1403 (6)	-.1451 (4)	.2029 (3)	.0844	.0695	.1761	-.0149	.0169	.0327
N 1	.0835 (4)	-.0586 (3)	.1630 (1)	.0611	.0537	.0738	-.0063	-.0080	-.0060
O(C) 1	.2327 (3)	.1676 (2)	.1631 (1)	.0456	.0897	.0611	.0085	-.0040	.0224
O(H) 1	.1824 (3)	.1024 (2)	.2563 (1)	.0490	.0897	.0446	-.0043	.0070	.0093

	x	y	z	B(Å^2)
H2	.382 (3)	.238 (2)	.580 (1)	6.1
H3	.656 (3)	.210 (2)	.569 (1)	6.9
H4	.752 (3)	.135 (3)	.478 (1)	7.0
H5	.725 (3)	.069 (3)	.381 (1)	7.1
H6	.560 (4)	.016 (3)	.294 (1)	7.0
H7	.276 (3)	.024 (2)	.305 (1)	4.2
H1(CM1)	.164 (4)	.360 (3)	.478 (2)	10.3
H2(CM1)	.170 (4)	.345 (3)	.555 (2)	9.6
H3(CM1)	-.002 (4)	.327 (3)	.518 (1)	7.6
H1(CM2)	.105 (4)	.057 (3)	.553 (2)	9.4
H2(CM2)	-.028 (3)	.154 (2)	.562 (1)	5.4
H3(CM2)	.145 (3)	.163 (3)	.601 (1)	7.8
H(N)	.074 (4)	.176 (3)	.466 (1)	8.2
H2 1	.147 (3)	-.196 (2)	.148 (1)	6.7
H3 1	.425 (4)	-.161 (3)	.151 (2)	8.6
H4 1	.530 (4)	.010 (2)	.162 (1)	6.9
H5 1	.484 (4)	.201 (3)	.181 (1)	7.1
H6 1	.307 (3)	.341 (3)	.204 (1)	7.4
H7 1	.025 (3)	.308 (2)	.214 (1)	6.8
H1(CM1)1	-.105 (5)	-.003 (3)	.075 (2)	12.1
H2(CM1)1	-.264 (4)	-.068 (3)	.100 (2)	10.2
H3(CM1)1	-.106 (4)	-.134 (3)	.077 (2)	12.5
H1(CM2)1	-.098 (4)	-.135 (3)	.245 (2)	11.9
H2(CM2)1	-.105 (5)	-.213 (3)	.185 (2)	12.8
H3(CM2)1	-.261 (4)	-.141 (3)	.204 (2)	10.5
H(O)	-.085 (5)	.085 (3)	.289 (2)	12.8

possible proton arrangements within a given dimer must then be nearly isoenergetic, and hence statistical disorder between them can be expected. The proton position listed in *Table 9* is 0.94 Å from $\mathrm{O_H}$ (1.77 Å from $\mathrm{O_C}$, but its isotropic temperature factor of $B=8\pi^2u^2=18.6$ Å^2 ($u=0.48$ Å) shows that it is not localized at this position.

Crystal Structure of *N,N*-Dimethyl-8-methoxynaphthalene-1-carboxamide (2f). – Atomic parameters are listed in *Table 10*, bond lengths and angles are shown in *Figure 21*, and stereoviews of the molecule and of the packing in the crystal are shown in *Figures 22* and *23* respectively. This structure determination is less accurate than most of the others because of the limited amount of data available (*cf.* **2d**), and no thermal motion analysis was carried out. However, the deformations of the amide group are large, and Δ_N is in the opposite sense to Δ_C, as described for the following structure **2g**.

Table 7. *Compound* **2c**: *positional and vibrational parameters* (see caption to *Table 5*)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	-.1855 (4)	.3849 (3)	.1711 (2)	.0445	.0386	.0420	.0035	.0035	-.0039
C2	-.2440 (5)	.3707 (3)	.0852 (2)	.0650	.0538	.0465	.0040	.0003	.0009
C3	-.3893 (6)	.2965 (4)	.0650 (2)	.0700	.0677	.0478	.0051	-.0132	-.0061
C4	-.4703 (5)	.2335 (3)	.1299 (3)	.0478	.0585	.0712	.0040	-.0134	-.0107
C5	-.5069 (5)	.1818 (4)	.2899 (3)	.0476	.0791	.0762	-.0120	.0122	.0065
C6	-.4629 (6)	.2007 (5)	.3774 (3)	.0599	.0970	.0672	-.0073	.0233	.0185
C7	-.3314 (6)	.2874 (4)	.3990 (2)	.0624	.0819	.0431	.0091	.0082	.0048
C8	-.2405 (4)	.3490 (3)	.3345 (2)	.0426	.0505	.0411	.0106	.0029	-.0009
C9	-.2803 (4)	.3274 (3)	.2420 (2)	.0394	.0410	.0410	.0077	.0022	-.0008
C10	-.4193 (4)	.2464 (3)	.2206 (3)	.0403	.0533	.0589	.0058	.0003	-.0027
C(M1)	.1270 (6)	.3780 (4)	.1806 (3)	.0517	.0679	.0913	.0060	-.0047	-.0144
C(M2)	-.0143 (6)	.5721 (4)	.1522 (3)	.0696	.0562	.1016	-.0088	.0114	.0132
C(E)	.1747 (8)	.4823 (5)	.4133 (4)	.0764	.0955	.1017	-.0119	-.0337	-.0078
C(C)	-.1121 (5)	.4453 (3)	.3624 (2)	.0625	.0552	.0342	.0070	-.0031	-.0036
O(E)	.0403 (4)	.3957 (2)	.3876 (2)	.0641	.0595	.0657	-.0014	-.0185	-.0004
O(C)	-.1492 (5)	.5520 (2)	.3719 (2)	.0911	.0532	.0674	.0150	-.0062	-.0209
N	-.0308 (4)	.4506 (3)	.1940 (2)	.0461	.0447	.0498	.0012	.0095	-.0032

	x	y	z	B(Å^2)
H2	-.171 (6)	.412 (4)	.038 (3)	5.0
H3	-.429 (6)	.296 (4)	.001 (3)	6.2
H4	-.565 (7)	.173 (5)	.122 (3)	7.6
H5	-.591 (7)	.105 (4)	.271 (3)	5.9
H6	-.500 (11)	.137 (6)	.429 (5)	11.0
H7	-.303 (5)	.300 (4)	.457 (2)	4.5
H1(CE)	.274 (9)	.443 (6)	.410 (4)	8.7
H2(CE)	.190 (10)	.551 (7)	.368 (5)	10.5
H3(CE)	.137 (11)	.497 (8)	.475 (6)	12.9
H1(CM1)	.215 (6)	.422 (4)	.207 (3)	5.6
H2(CM1)	.112 (9)	.288 (6)	.216 (4)	9.9
H3(CM1)	.146 (7)	.356 (5)	.115 (4)	7.2
H1(CM2)	.010 (11)	.556 (7)	.094 (5)	11.7
H2(CM2)	-.131 (10)	.626 (7)	.161 (5)	10.1
H3(CM2)	.085 (6)	.624 (4)	.187 (3)	5.8

Table 8. *Compound* **2d**: *positional and vibrational parameters* (see caption to *Table 5*)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	-.1968 (11)	.3190 (9)	-.1980 (14)	.0602	.0594	.0548	-.0030	.0238	-.0094
C2	-.1323 (13)	.3762 (10)	-.3293 (14)	.0879	.0798	.0458	-.0038	.0319	.0108
C3	.0422 (15)	.3754 (12)	-.2848 (17)	.1071	.0892	.0875	-.0152	.0689	.0093
C4	.1474 (12)	.3159 (11)	-.1219 (16)	.0816	.0800	.0803	-.0051	.0559	.0014
C5	.1953 (12)	.1924 (10)	.1916 (14)	.0646	.0668	.0810	.0053	.0199	.0142
C6	.1341 (13)	.1357 (12)	.3209 (15)	.0717	.1028	.0883	.0204	.0225	.0318
C7	-.0371 (13)	.1358 (11)	.2888 (15)	.0699	.1031	.0575	.0111	.0314	.0114
C8	-.1497 (10)	.1924 (8)	.1183 (12)	.0556	.0520	.0518	-.0131	.0191	-.0055
C9	-.0880 (12)	.2535 (10)	-.0239 (13)	.0531	.0524	.0441	.0053	.0224	-.0017
C10	.0864 (11)	.2535 (9)	.0168 (13)	.0582	.0556	.0655	-.0155	.0288	-.0051
C(M)	-.4781 (11)	.3898 (10)	-.3837 (13)	.0691	.1016	.0676	.0055	.0104	.0134
C(C)	-.3285 (11)	.1731 (9)	.0935 (13)	.0551	.0611	.0398	-.0028	.0168	.0112
C(K)	-.4277 (13)	.0516 (9)	-.0355 (13)	.0943	.0749	.0702	-.0286	.0362	-.0258
O(M)	-.3588 (0)	.3223 (6)	-.2192 (0)	.0589	.1001	.0467	.0118	.0190	.0205
O(C)	-.3922 (9)	.2465 (6)	.1893 (10)	.0730	.0798	.0607	.0016	.0361	-.0081

	x	y	z	B(Å^2)
H2	-.209 (0)	.420 (0)	-.453 (0)	8.0
H3	.087 (0)	.170 (0)	-.380 (0)	8.0
H4	.270 (0)	.317 (0)	-.096 (0)	8.0
H5	.317 (0)	-.058 (0)	.219 (0)	8.0
H6	.213 (0)	.091 (0)	.444 (0)	8.0
H7	-.080 (0)	-.156 (0)	.388 (0)	8.0
H1(CK)	-.554 (0)	.055 (0)	-.037 (0)	8.0
H2(CK)	-.369 (0)	-.304 (0)	.019 (0)	8.0
H3(CK)	-.427 (0)	.070 (0)	-.182 (0)	8.0
H1(CM)	-.601 (0)	.129 (0)	-.372 (0)	8.0
H2(CM)	-.476 (0)	.335 (0)	-.513 (0)	8.0
H3(CM)	-.446 (0)	.256 (0)	-.386 (0)	8.0

Crystal Structure of *N*, *N*-Dimethyl-8-hydroxynaphthalene-1-carboxamide (2g). – Atomic parameters are listed in *Table 11*, bond lengths and angles are shown in *Figure 24*, a stereoview of the molecule in *Figure 25*, and a packing drawing in *Figure 26*. The out-of-plane deformation of the amide group is not as large as in **2f**, but it can be measured more accurately, thanks to the better quality of the experimental data (see *Table 3*). The torsion angles between *cis*-oriented substituents are $\omega_1(CCNC_{13}) = -18.2°$, $\omega_2(OCNC_{12}) = -0.3°$, – *i.e.* whereas the $N-C_{13}$ bond is rotated by 18.2° out of the CCN plane, the N–C(12) bond lies

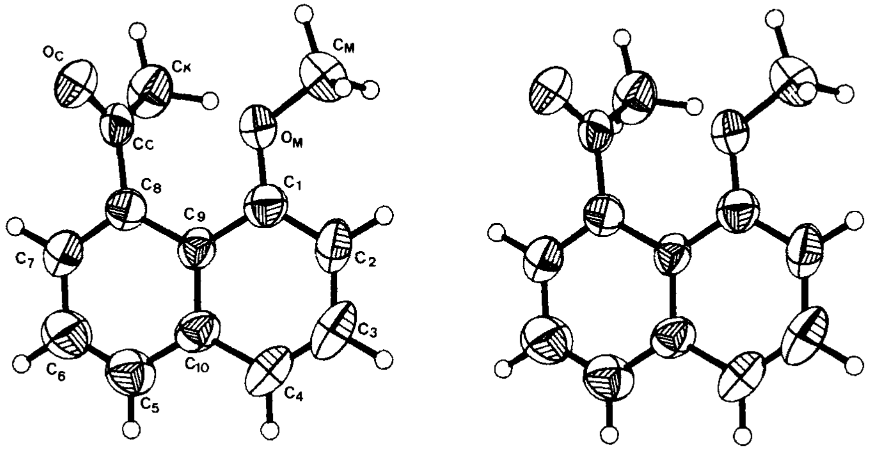


Fig. 15. *Stereoview of molecule* **2d**

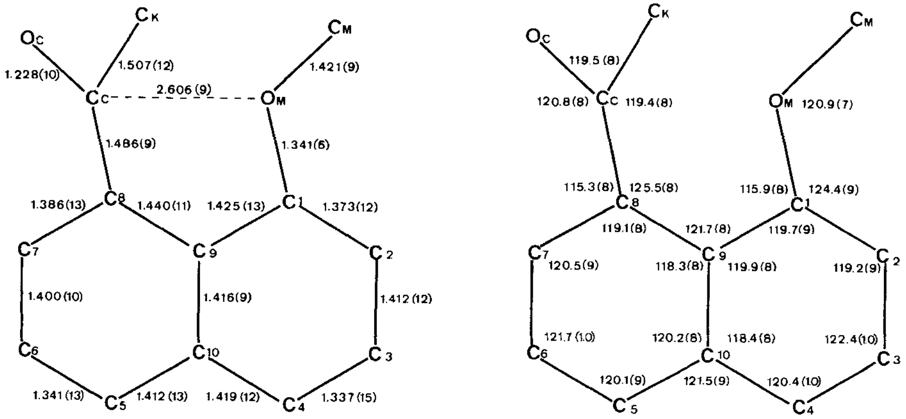


Fig. 16. *Bond lengths and angles in molecule* **2d**

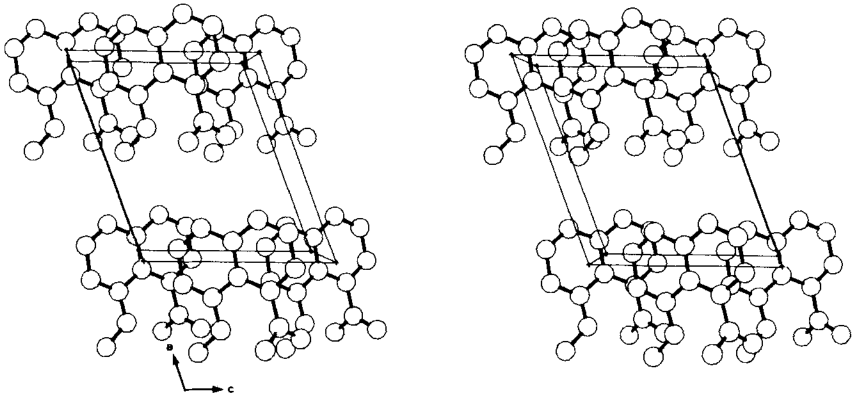


Fig. 17. *Crystal packing of compound* **2d**

Table 9. *Compound* **2e**: *positional and vibrational parameters* (see caption to *Table 5*)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	.1174 (1)	.4031 (6)	-.0235 (4)	.0473	.0730	.0595	.0023	-.0094	-.0021
C2	.1441 (2)	.5519 (8)	-.0635 (5)	.0776	.0687	.0835	-.0067	-.0072	.0111
C3	.1889 (2)	.5544 (8)	-.0203 (5)	.0814	.0809	.0995	-.0316	-.0028	.0107
C4	.2067 (1)	.4150 (7)	.0576 (4)	.0555	.0912	.0756	-.0180	-.0077	-.0004
C5	.1980 (1)	.1099 (7)	.1828 (4)	.0385	.1032	.0637	.0037	-.0108	.0046
C6	.1726 (1)	-.0372 (7)	.2254 (4)	.0518	.0944	.0775	.0115	-.0127	.0200
C7	.1272 (1)	-.0478 (7)	.1837 (4)	.0608	.0776	.0724	-.0112	-.0067	.0210
C8	.1086 (1)	.0896 (6)	.1014 (3)	.0356	.0668	.0465	-.0001	-.0032	.0031
C9	.1344 (1)	.2494 (6)	.0579 (3)	.0375	.0587	.0465	-.0003	-.0026	-.0068
C10	.1802 (1)	.2582 (6)	.1006 (3)	.0420	.0746	.0476	-.0033	-.0024	-.0029
C(C)	.0607 (1)	.0563 (6)	.0573 (4)	.0410	.0745	.0487	-.0053	-.0036	-.0038
C(M)	.0532 (3)	.5087 (15)	-.1520 (10)	.0981	.1164	.1586	.0186	-.0559	.0439
O(H)	.0307 (1)	.1078 (4)	.1372 (2)	.0390	.1438	.0681	.0012	.0012	-.0239
O(C)	.0533 (1)	-.0271 (5)	-.0516 (3)	.0496	.1598	.0931	.0010	-.0131	-.0613
O(M)	.0733 (1)	.3839 (4)	-.0560 (3)	.0547	.1040	.1143	.0001	-.0285	.0453

	x	y	z	B(Å²)
H2	.129 (1)	.652 (7)	-.120 (5)	6.3
H3	.206 (1)	.662 (5)	-.050 (3)	7.7
H4	.240 (1)	.417 (6)	.092 (4)	8.6
H5	.230 (1)	.120 (4)	.216 (3)	6.8
H6	.185 (1)	-.132 (5)	.291 (4)	9.5
H7	.110 (1)	-.154 (5)	.215 (3)	5.6
H1(CM)	.059 (2)	.627 (8)	-.129 (6)	15.1
H2(CM)	.071 (1)	.506 (7)	-.230 (4)	16.1
H3(CM)	.022 (2)	.477 (9)	-.149 (6)	13.7
H(OH)	-.007 (2)	.091 (7)	.087 (4)	19.8

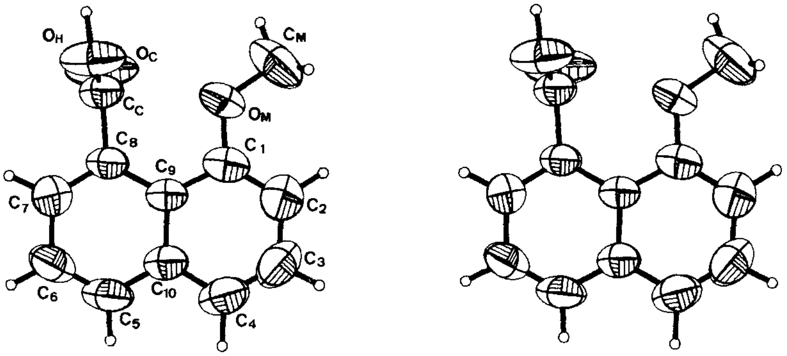


Fig. 18. *Stereoview of molecule* **2e**

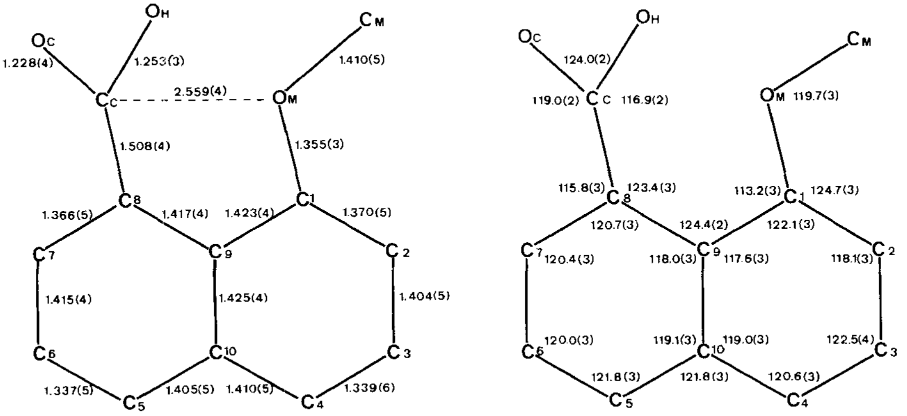


Fig. 19. *Bond lengths and angles in molecule* **2e**

Table 10. *Compound* **2f**: *positional and vibrational parameters* (see caption to *Table 5*)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	.4088 (3)	.3140 (4)	.7309 (3)	.0633	.0726	.0659	.0092	-.0022	.0073
C2	.3711 (3)	.3706 (4)	.8040 (3)	.0898	.0924	.0807	.0223	.0027	.0033
C3	.2884 (4)	.3359 (6)	.8375 (3)	.0902	.1527	.0885	.0243	.0033	.0038
C4	.2461 (3)	.2470 (6)	.8001 (4)	.0634	.1435	.0917	.0205	.0129	.0397
C5	.2447 (3)	.0880 (5)	.6821 (5)	.0581	.1061	.1361	-.0152	-.0120	.0580
C6	.2817 (3)	.0305 (4)	.6106 (5)	.0813	.0738	.1480	-.0250	-.0463	.0260
C7	.3639 (3)	.0658 (3)	.5729 (3)	.0794	.0591	.1015	-.0095	-.0248	.0057
C8	.4057 (2)	.1579 (3)	.6101 (3)	.0634	.0512	.0670	-.0015	-.0067	.0116
C9	.3687 (3)	.2178 (3)	.6866 (3)	.0525	.0660	.0651	.0025	-.0097	.0174
C10	.2850 (3)	.1836 (4)	.7231 (4)	.0560	.0862	.0996	-.0033	-.0116	.0393
C11	.4960 (3)	.1828 (4)	.5687 (3)	.0745	.0605	.0688	-.0107	.0009	-.0059
C12	.5849 (3)	.2908 (4)	.4596 (3)	.1063	.1193	.1334	-.0195	.0516	.0063
C13	.4270 (3)	.3393 (3)	.4786 (3)	.1113	.0798	.0861	-.0105	-.0107	.0260
C14	.5364 (3)	.4336 (4)	.7382 (3)	.0960	.0957	.1157	-.0267	-.0169	-.0185
N1	.4990 (2)	.2611 (3)	.4998 (3)	.0822	.0672	.0765	-.0178	.0076	-.0011
O1	.4892 (2)	.3433 (2)	.6944 (2)	.0743	.0841	.0896	-.0175	.0031	-.0181
O2	.5595 (2)	.1261 (2)	.5937 (2)	.0663	.0809	.1248	.0043	-.0026	.0055

	x	y	z	B(Å^2)
H2	.399 (2)	.442 (2)	.831 (2)	8.5
H3	.262 (2)	.380 (3)	.896 (3)	12.9
H4	.190 (2)	.210 (3)	.824 (2)	10.3
H5	.192 (2)	.068 (2)	.711 (2)	9.1
H6	.256 (2)	-.036 (2)	.577 (2)	7.7
H7	.391 (2)	.020 (2)	.517 (2)	7.9
H121	.575 (3)	.288 (4)	.397 (3)	15.0
H122	.602 (5)	.366 (7)	.478 (5)	26.1
H123	.625 (2)	.224 (3)	.466 (3)	11.0
H131	.427 (2)	.351 (2)	.412 (2)	8.5
H132	.365 (2)	.310 (3)	.503 (2)	9.6
H133	.437 (3)	.414 (4)	.507 (3)	14.2
H141	.500 (3)	.504 (3)	.723 (2)	11.9
H142	.543 (2)	.417 (3)	.801 (3)	11.7
H143	.588 (2)	.442 (3)	.699 (2)	10.2

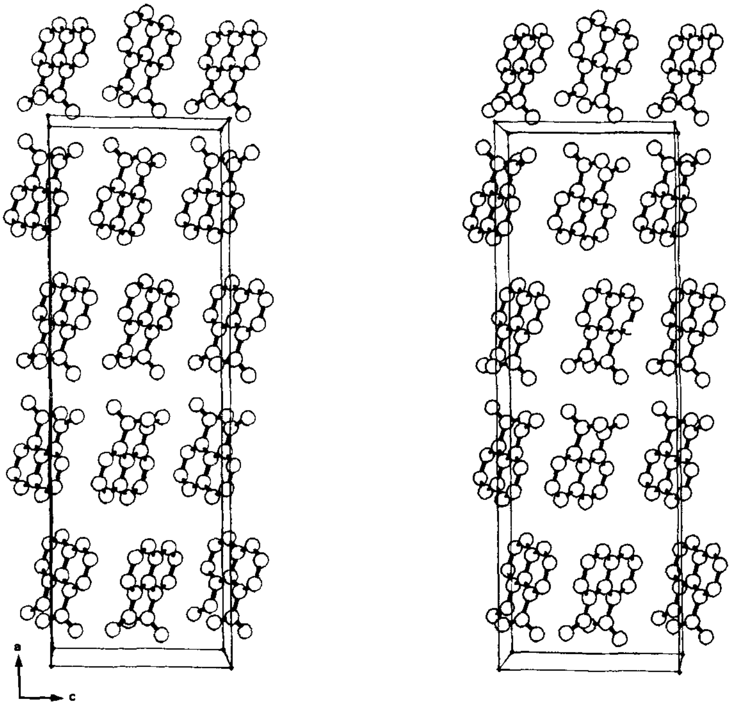


Fig. 20. *Crystal packing of compound* **2e**

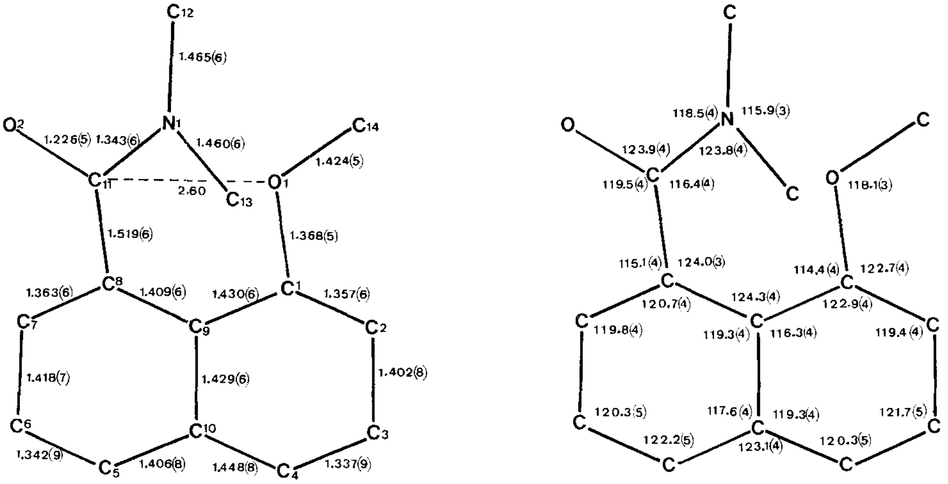


Fig. 21. *Bond lengths and angles in molecule* **2f**

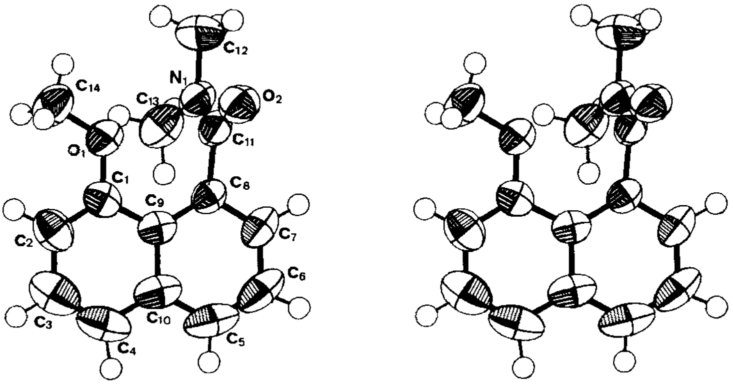


Fig. 22. *Stereoview of molecule* **2f**

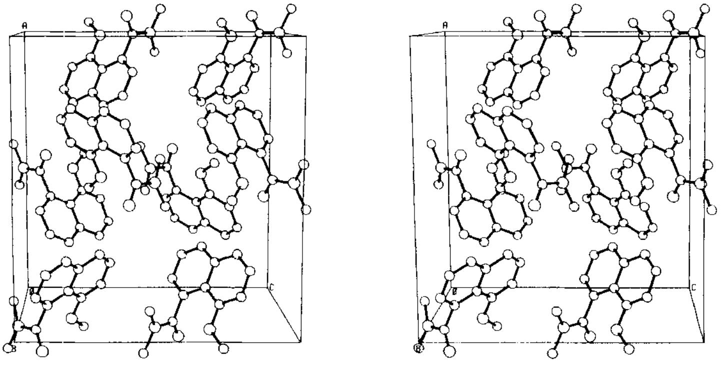


Fig. 23. *Crystal packing of compound* **2f**

precisely *syn*-planar to the C=O bond. These relationships are strikingly similar to those that pertain in nonplanar enamines [24].

Analysis of the vibrational parameters in terms of the rigid-body criterion gives $\langle \Delta^2_{AB} \rangle^{1/2}_{bonds} = 0.0030$ Å^2, the lowest obtained in this series. The large Δ_{AB} values all involve the methyl carbon atom C(13), the methyl that is *trans* to the amide oxygen atom; $\langle \Delta^2_{AB} \rangle^{1/2}$ is 0.0038 Å^2 for the 89 nonbonded pairs not involving C(13) and it is 0.0194 Å^2 for the 10 nonbonded pairs involving this atom and the atoms of the naphthalene skeleton. This analysis shows that any attempt to explain the observed U_{ij} values in terms of rigid-body motion would be in vain. Out of several models incorporating nonrigid motion that were tested, two merit special mention: model 1 involves a torsional vibration of the entire amide group around the (C(8)–C)-bond; model 2 involves vibration only of C(13) in the direction normal to the C(11)NC(13) plane (this motion can be simulated by torsion around the (C(11)–N)-bond with the motion imparted only to C(13)). Both models give almost the same level of agreement: $R(U_{ij}) = 0.104$ for model 1 (torsional amplitude 4.9° (0.6°)) and $R = 0.108$ for model 2 (torsional amplitude 9.1° (1.3°)). The motion of C(13) in model 2 is analogous to the nitrogen inversion process in nonplanar enamines, which involves mainly a motion of the nitrogen substituent *anti* to the double bond [24].

NMR. Spectra. - At about 37° the NMR. spectra (100 MHz) of **2a**, **2b** and **2c** each show a single peak for the two amino CH_3 groups. In the case of the amino ketone **2a** this peak is broad (at (37°). As the temperature is lowered the peak broadens further and eventually splits into two peaks, which are sharp at $-36°$ ($\Delta\delta \sim 0.5$ ppm). A rough analysis of the spectra gives an activation energy of about 14.0 kcal mol^{-1} for the exchange process. The amino ester **2c** shows a similar effect, but the peak broadening is not so pronounced.

Table 11. *Compound* **2g**: *positional and vibrational parameters* (see caption to *Table 5*)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	.5715 (2)	.4175 (1)	.2646 (3)	.0326	.0387	.0382	.0029	-.0009	.0032
C2	.6071 (3)	.3930 (2)	.1054 (3)	.0467	.0596	.0368	-.0001	.0037	.0027
C3	.5492 (3)	.3175 (2)	.0411 (3)	.0606	.0731	.0412	.0067	-.0015	-.0152
C4	.4567 (3)	.2685 (1)	.1319 (3)	.0543	.0512	.0561	.0010	-.0106	-.0178
C5	.3219 (3)	.2411 (1)	.3955 (4)	.0447	.0371	.0705	-.0103	-.0114	-.0005
C6	.2876 (3)	.2634 (2)	.5542 (4)	.0434	.0523	.0700	-.0195	-.0027	.0194
C7	.3486 (2)	.3367 (1)	.6249 (3)	.0386	.0547	.0448	-.0083	.0055	.0039
C8	.4430 (2)	.3875 (1)	.5356 (3)	.0248	.0347	.0396	-.0015	.0004	.0029
C9	.4775 (2)	.3672 (1)	.3663 (2)	.0254	.0311	.0379	.0022	-.0041	.0023
C10	.4178 (2)	.2915 (1)	.2965 (3)	.0329	.0366	.0492	.0016	-.0103	-.0033
C11	.5156 (2)	.4576 (1)	.6306 (3)	.0329	.0382	.0316	-.0019	.0054	.0009
C12	.4985 (3)	.5947 (1)	.7627 (4)	.0716	.0484	.0726	.0037	.0045	-.0228
C13	.3122 (3)	.5520 (2)	.5519 (4)	.0593	.0664	.0876	.0239	-.0164	-.0110
N1	.4400 (2)	.5294 (1)	.6530 (2)	.0425	.0428	.0491	.0050	.0028	-.0090
O1	.6212 (2)	.4909 (1)	.3328 (2)	.0525	.0423	.0507	-.0161	.0181	-.0026
O2	.6363 (2)	.4434 (1)	.6996 (2)	.0395	.0423	.0530	-.0018	-.0121	-.0037

	x	y	z	B(Å^2)
H2	.672 (5)	.426 (3)	.049 (5)	8.9
H3	.580 (4)	.299 (2)	-.070 (5)	7.2
H4	.424 (4)	.217 (2)	.086 (4)	5.6
H5	.284 (3)	.188 (2)	.348 (4)	4.4
H6	.224 (3)	.229 (2)	.620 (3)	4.5
H7	.324 (3)	.355 (2)	.738 (4)	4.6
H121	.565 (4)	.571 (2)	.853 (4)	7.7
H122	.575 (4)	.631 (2)	.701 (5)	8.6
H123	.427 (4)	.628 (2)	.796 (5)	8.2
H131	.290 (4)	.513 (2)	.473 (4)	7.7
H132	.232 (6)	.550 (3)	.609 (7)	15.1
H133	.317 (7)	.606 (3)	.498 (7)	13.9
H(O)	.693 (3)	.510 (2)	.273 (4)	5.2

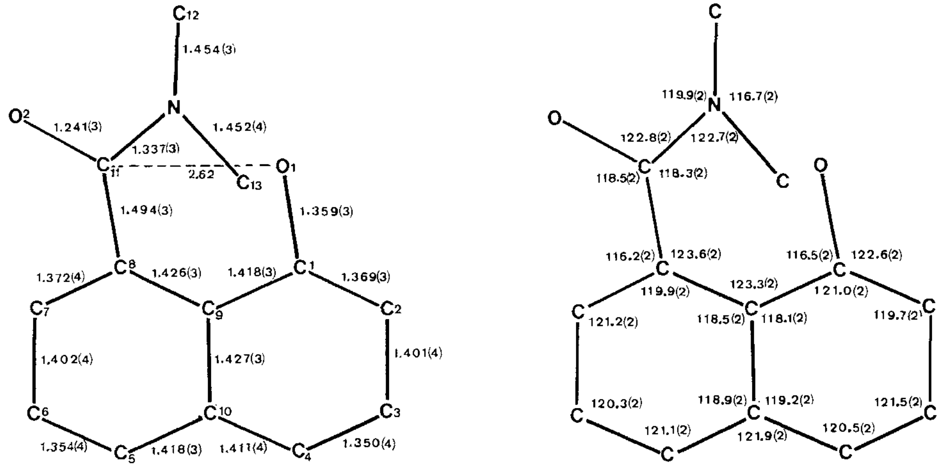


Fig. 24. *Bond lengths and angles in molecule* **2g**

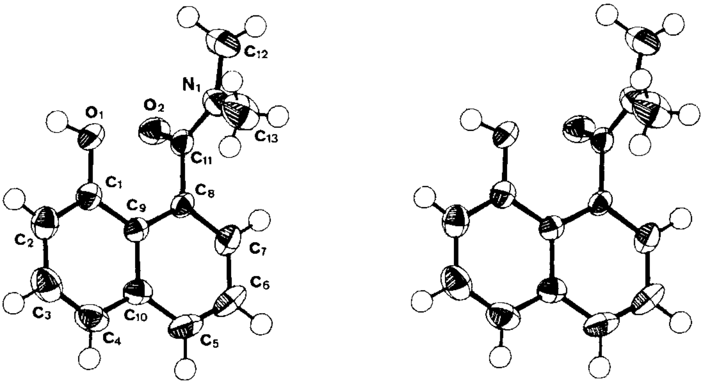


Fig. 25. *Stereoview of molecule* **2g**

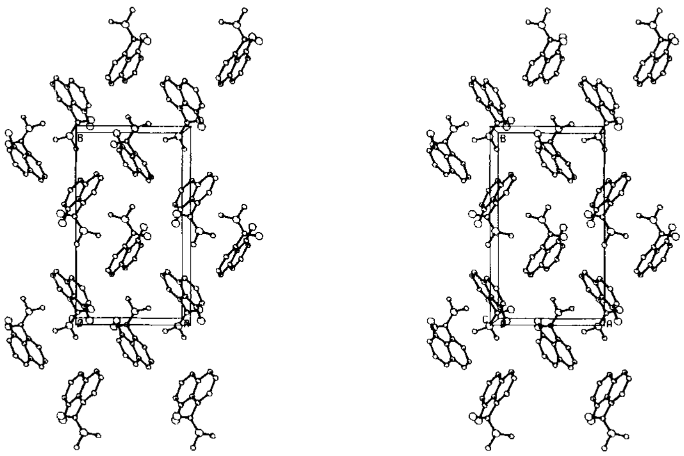
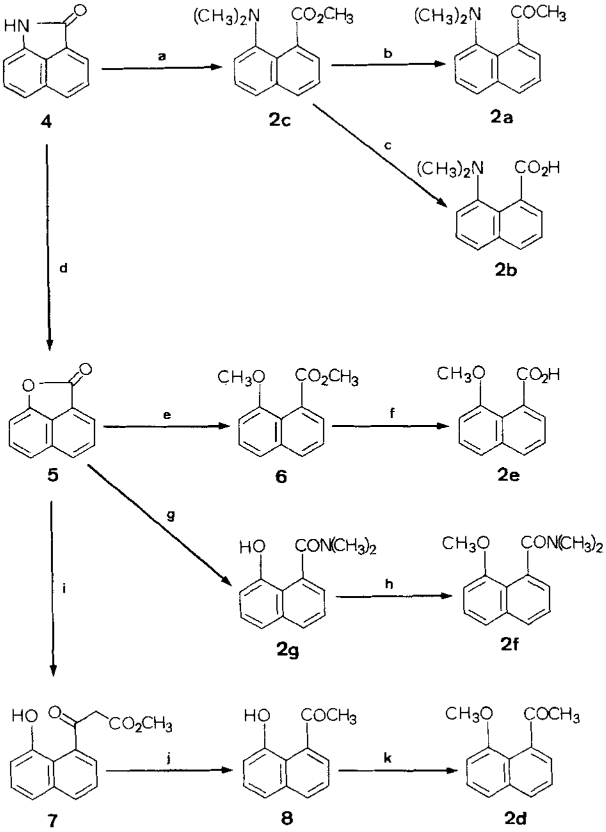


Fig. 26. *Crystal packing of compound* **2g**

The predominant tautomer of **2b** in $CDCl_3$ and D_2O is the zwitterion[7], in which the two amino CH_3 groups are equivalent (see crystal structure of **2b**).

Syntheses. - A brief outline of the synthetic routes is shown in the *Scheme*. The significance of the letter symbols is as follows: **a)** (i) Reflux 0.5N NaOH, 2 h, evaporate. (ii) Reflux $MeI/K_2CO_3/MeOH$, 2h. Yield, 66.5% from **4**. **b)** $MeLi/Et_2O$, 0°, 2h; RT. 6h. Yield 57% from **2c**. **c)** Reflux 2N HCl, 3h. Yield 71% from **2c**. **d)** See [26]. **e)** (i) Reflux NaOMe/MeOH 4h, evaporate. (ii) Reflux $MeI/K_2CO_3/Me_2CO$, 4h. Yield 62% from **5**. **f)** Reflux $NaOH/H_2O/EtOH$, 8h. Yield 65% from **6**. **g)** $Me_2NH/MeOH$, 3h. RT. Yield 86% from **5** (no chromatography). **h)** Reflux MeONa/MeI/MeOH, 2h. Yield 81% from **2g**. **i)** $BrCH_2CO_2Et/Zn/THF$, 3.5h, RT., reflux 1h. Yield 70% from **5**. **j)** Reflux N NaOH, acidify (pH 3); boil precipitate with water 10 min. Yield 71% from **7**. **k)** $MeI/K_2CO_3/Me_2CO$, RT., 21h. Yield 60% from **8**.



Usual conditions and standard work-up procedures were used throughout. Crude products were usually purified by column chromatography on silica gel or by preparative TLC., followed by sublimation (if necessary) and crystallization. The quoted yields refer to pure material. Lactam **4** was prepared by two methods [25], [26]; the latter is more suitable for large scale preparations.

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[7] The peak (2.96 δ) from the amino CH_3 groups is 0.35 ppm lower than for **2a** and **2c**. An aromatic proton appears at low field (8.57 δ, $d \times d$, $J \sim 7$ Hz and ~ 2 Hz); this is probably H−C(7) which is deshielded by the carboxylate group (coplanar with the naphthalene ring in the zwitterion; see *Fig. 9*).

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