

Tableau 3. Distances et angles de quelques liaisons hydrogène intramoléculaires

Composé ou complexe	C—O...H (Å)	C—O...H (°)	O...O (Å)	O—H (Å)	O—H...O (°)	Référence
Acide vulpinique	1,54 (6)	116 (5)	2,513 (5)	0,98 (6)	168 (5)	
Acide salicylique— nicotine	1,549	110,4	2,544	1,147	140,8	(a)
Atranorine	1,64 (7) 1,66 (7)	95 (5) 99 (5)	2,525 (5) 2,521 (5)	0,99 (7) 0,92 (7)	158 (5) 153 (5)	(b)
Acide salicylique— antipyrine	1,67 (13)	103,5	2,581	0,987	150,7	(c)
Acide salicylique (rayons X)	1,704	106,2	2,620	1,029	145,8	(d)
(neutrons)	1,766	107,1	2,608	0,957	145,4	(e)

Références: (a) Kim & Jeffrey (1971); (b) Brassy, Bachet, Bodo & Molho (1982); (c) Singh & Vijayan (1974); (d) Sundaralingam & Jensen (1965); (e) Bacon & Jude (1973).

(Magomedova, Dzyabchenko, Zavodnik & Belsky, 1980); 81,9° dans le cas de l'hydroxy-5 phényl-1 (phtalimidoéthyle-1)-3 pyrazolecarboxylate-4 de méthyle (Sikirica & Vicković, 1980)]. Les atomes C(1), O(2), C(3), O(4), C(5) du groupement acétyle sont presque dans le plan du furylidène comme leurs distances respectives à ce plan [0,02 (1); 0,00 (1); 0,06 (1); 0,12 (1); 0,03 (1) Å] le montrent. Par contre le furylidène et le phényle C(6)—C(11) ne sont pas coplanaires, puisque l'angle dièdre de leurs plans vaut 69 (1)°. La quasi planéité d'une grande partie de la molécule et les longueurs des liaisons C(5)—C(12) 1,353 (6) Å, C(16)—C(19) 1,469 (7) Å montrent que le groupement acétyle, le furylidène et le phényle C(19)—C(24) sont conjugués, ce qui permet d'expliquer la coloration jaune de l'acide vulpinique.

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Structure of Acetanilide (C₈H₉NO) at 113 K*

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Abstract. $M_r = 135.2$, $Pbca$, $a = 19.509$ (11), $b = 9.364$ (8), $c = 7.778$ (10) Å, $V = 1421.0$ Å³, $Z = 8$,

$D_x = 1.264$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.79$ cm⁻¹, $F(000) = 576$, $T = 113$ K. Final $R = 0.033$ for 1301 observed reflections. The structure has been redetermined at low temperature in order to verify if structural reorganization of the molecule is responsible for certain changes in the vibrational spectrum which

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occur upon cooling. The largest difference occurs in the carbonyl C—O [1.234 (2) Å] bond length, which increases by 0.015 (4) Å.

Introduction. The room-temperature X-ray structure determination of acetanilide was reported in 1954 (Brown & Corbridge, 1954). Further refinement on these same data was described several years later (Brown, 1966). Recently acetanilide has become the center of some interest due to certain anomalous properties which may arise as a consequence of soliton behavior. Thus, an absorption at 1650 cm^{-1} in the vibrational spectrum has been assigned to a soliton which results from coupling of the amide-I vibration to an out-of-plane displacement of the hydrogen-bonded proton (Careri, Buontempo, Carta, Gratton & Scott, 1983). The peak at 1650 cm^{-1} appears only as the molecule is cooled and is well formed at 140 K. (The room-temperature amide-I absorption occurs at $\sim 1665\text{ cm}^{-1}$.) We have therefore undertaken a single-crystal X-ray diffraction analysis of acetanilide below this temperature in order to explore the possibility that the new absorption results from a structural change upon cooling. Our results appear below.

Experimental. Acetanilide (99.99%) was purchased from G. Frederick Smith Company. Suitable crystals were grown by vacuum sublimation. Crystal dimensions $0.2 \times 0.2 \times 0.3\text{ mm}$. D_m not measured. Enraf-Nonius CAD-4 diffractometer. The space group (*Pbca*) is uniquely defined by the systematic absences. Cell constants from 25 reflections with $16.0 \leq \theta \leq 22.0^\circ$. No absorption correction. $2\theta_{\text{max}} = 60^\circ$. Range of *hkl*: 0–27, 0–13, 0–10. 717 and 12,7,0 measured periodically, approximately 8% average increase in intensity observed, polynomial correction applied. 2063 unique reflections measured, 1301 with $I > 3.0\sigma(I)$. Function minimized: $\sum w(|F_o| - |F_c|)^2$, $w = 1/[\sigma_c^2(F) + 0.015F^2]$; $\sigma_c^2(F)$ is based on counting statistics; refinement on *F*. Initial coordinates taken from Brown & Corbridge (1954). The final model included anisotropic temperature factors for all nonhydrogen atoms, positional and isotropic thermal parameters for H atoms and an isotropic correction for secondary extinction (128 parameters). Final $R = 0.033$, $wR = 0.036$, $S = 2.22$, $(A/\sigma)_{\text{max}} = 0.01$. $\Delta\rho$ max./min. was $0.28/-0.18\text{ e \AA}^{-3}$. The mosaic block size parameter was $5.3 (12) \times 10^{-6}\text{ mm}$. The programs used were principally those of Dr A. C. Larson (Larson, 1977); neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). Positional and thermal parameters are listed in Table 1.*

Discussion. Fig. 1 depicts a view of the molecule in which important interatomic distances from the room-temperature (Brown, 1966) and present ($T = 113\text{ K}$) study are compared. We have observed only one significant structural change in acetanilide upon cooling. At low temperature there is a lengthening of the carbonyl C(7)—O distance by 0.015 Å; the discrepancy here is significant at the 4σ level. As a result the hydrogen bonded N—H...O' distance is shortened by 0.029 \AA to $2.914 (3)\text{ \AA}$. All other distances differ by less than 3σ . Differences in interatomic angles are even smaller: the largest discrepancy occurring in the amide side chain of the molecule is only 0.2° .

Our low-temperature structural analysis of the acetanilide molecule has allowed a more precise determination of H-atom parameters and, in particular,

Table 1. Fractional coordinates and thermal parameters (\AA^2) for acetanilide

	x	y	z	B or B_{eq}
C(1)	0.4080 (1)	0.0722 (1)	0.1271 (2)	1.47*
C(2)	0.3551 (1)	-0.0227 (1)	0.1681 (2)	1.75*
C(3)	0.2891 (1)	0.0022 (2)	0.1091 (2)	1.96*
C(4)	0.2752 (1)	0.1212 (1)	0.0082 (2)	1.99*
C(5)	0.3280 (1)	0.2123 (1)	-0.0369 (2)	1.96*
C(6)	0.3945 (1)	0.1889 (1)	0.0210 (2)	1.66*
C(7)	0.5275 (1)	0.1319 (1)	0.2124 (2)	1.55*
C(8)	0.5889 (1)	0.0721 (2)	0.3042 (2)	2.03*
N(1)	0.4734 (1)	0.0420 (1)	0.1975 (1)	1.57*
O(1)	0.5271 (0)	0.2554 (1)	0.1567 (1)	2.05*
H(1)	0.4780 (7)	-0.0455 (16)	0.2427 (21)	2.38 (35)
H(2)	0.3653 (7)	-0.1041 (15)	0.2379 (17)	1.21 (28)
H(3)	0.2523 (8)	-0.0657 (16)	0.1399 (18)	2.12 (32)
H(4)	0.2279 (8)	0.1409 (15)	-0.0290 (18)	1.82 (30)
H(5)	0.3190 (7)	0.2963 (15)	-0.1099 (19)	1.62 (30)
H(6)	0.4311 (7)	0.2525 (16)	-0.0108 (19)	1.69 (28)
H(7)	0.5957 (8)	0.1291 (18)	0.4096 (24)	3.09 (37)
H(8)	0.6309 (9)	0.0871 (18)	0.2328 (22)	3.17 (38)
H(9)	0.5852 (8)	-0.0291 (18)	0.3333 (22)	2.75 (36)

$$* B_{\text{eq}} = \frac{1}{3} \sum B_{ii}$$

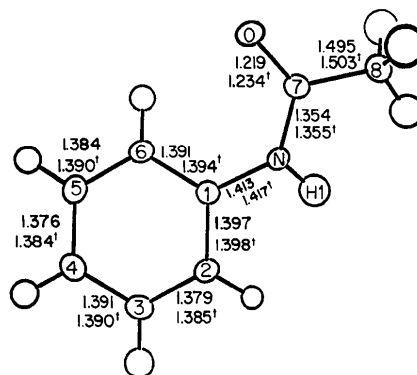


Fig. 1. View of the molecule comparing selected bond lengths (\AA). Those values with daggers (\dagger) are derived from the present analysis and each is subject to a mean estimated standard deviation (e.s.d.) of 0.002 \AA ; those without are from the room-temperature study (Brown, 1966), and are subject to a mean e.s.d. of 0.0034 \AA .

* Lists of calculated and observed structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39961 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

those of the amide proton, H(1). We note the following important features:

(1) The observed N–H(1) bond length of 0.90 (2) Å is reasonable for a distance determined by X-rays (Churchill, 1973).

(2) The steric interaction between the phenyl and acetyl groups is reflected in the angles subtended at the N atom, with C(1)–N–H(1) = 115 (1)° and C(7)–N–H(1) = 117 (1)°. The C(1)–N–C(7) angle is 127.6 (1)°.

(3) The hydrogen bond is, as expected, nearly linear, with N–H(1)–O' = 171 (1)°. The intermolecular H(1)⋯O' distance is 2.02 (2) Å.

In conclusion, we have shown that the temperature dependency of the vibrational spectrum of acetanilide results from factors unrelated to gross structural changes in crystals of the molecule, e.g. phase changes. It is interesting to note that the largest difference [0.015 (4) Å] between room- and low-temperature molecular species occurs in the carbonyl bond and that an increase in the C–O distance, while not inconsistent

with the amide-I shift to lower frequency at low temperature (Careri *et al.*, 1983), would not explain the appearance of two amide-I frequencies.

We plan to carry out further studies, especially single-crystal neutron analyses, on isotopically substituted species, to determine if there is a structural basis for additional spectral anomalies (Johnston & Swanson, 1984) that occur in these molecules.

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Synthesis and Structure of (*E*)-3-Fluoro-4-pyridinecarbaldehyde Oxime, C₆H₅FN₂O, and Conversion to its Quaternary Methyl Iodide Derivative

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Abstract. $M_r = 140.12$, monoclinic, $P2_1/a$, $a = 14.225$ (2), $b = 11.742$ (1), $c = 3.9852$ (6) Å, $\beta = 92.48$ (1)°, $V = 665.1$ (2) Å³, $Z = 4$, $D_x = 1.399$ g cm⁻³, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 9.148$ cm⁻¹, $F(000) = 288$, room temperature, $R = 0.050$ for 1217 independent observed reflections. Compound synthesized by oxidation of 3-fluoro- γ -picoline with iodine/dimethyl sulfoxide to give the corresponding aldehyde, which was then treated *in situ* with hydroxylamine. The oxime group and pyridine ring are coplanar but the fluorine atom does not participate in any hydrogen bonding. Quaternization with iodomethane gave (*E*)-3-fluoro-4-hydroxyiminomethyl-1-methylpyridinium iodide; this oxime group has a pK_a of 8.2, which is 0.4 pK_a units lower than that of the nonfluorinated parent compound, as expected from the electron-withdrawing effect of fluorine.

Introduction. Nucleophilic 1-alkyl-hydroxyiminomethylpyridinium halides (generally referred to as PAM compounds) reactivate phosphonate-inhibited acetylcholinesterase by attacking the phosphorus center of the phosphonate and displacing the free enzyme (Poziomek, Hackley & Steinberg, 1958). Thus, these compounds, such as 2-PAM, are potentially important as antidotes for chemical warfare agents involving phosphonate groups. Extensive studies (Hagedorn, Stark & Lorenz, 1972) indicate a pK_a optimum near 8.0–8.2 for the maximum rate of reactivation of enzyme, but the optimum structural parameters for most efficient reactivation have not yet been identified. The PAM compound 3-fluoro-4-hydroxyiminomethyl-1-methylpyridinium iodide (I) contains F substitution on the pyridine ring of the relatively slow enzyme reactivator 4-hydroxyiminomethyl-1-methylpyridinium