

This structural feature accounts for the (102) cleavage and for the great intensity of the 102 reflexion (64% of the theoretical maximum). Contact between adjacent molecules in a sheet is essentially edge-to-edge. The shortest intermolecular distances are between O and H; five such, shown in Fig. 1, range from 2.33 to 2.70 Å. One of these involves the hydroxyl H atom and can be described as a branch (albeit at 2.56 Å, a long one) of a bifurcated hydrogen bond. The others involve aromatic and ethylenic H atoms. Notwithstanding the equivocal reputation of the C—H...O bond (Donohue, 1968), it seems reasonable to describe the shorter of these interatomic vectors as weak bonds which mediate the sheet-like arrangement of the structure. It is suggested that the electron-withdrawing effect of the nitro and carbomethoxy groups is sufficient to induce significant acidic character in the H atoms involved.

Acta Cryst. (1975). B31, 1965

N-Carbomethoxyamino-3,6-dimethyl-4,5-diphenyl-2-pyridone

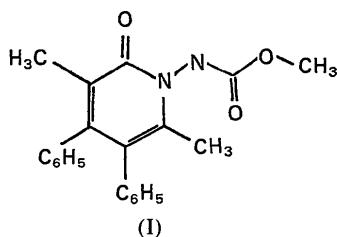
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(Received 11 November 1974; accepted 17 March 1975)

Abstract. C₂₁H₂₀N₂O₃, M.W. 348.41, monoclinic, *C*2/*c*, *a* = 16.127 (2), *b* = 6.835 (1), *c* = 34.553 (8) Å, β = 93.25 (2)°; *U* = 3802.4 (1.3) Å³; *d*_{meas} = 1.21, *d*_{calc} = 1.217 g cm⁻³, *Z* = 8. The final *R* was 0.040 for 1927 reflections used in the analysis. There is significant delocalization in the pyridone ring which is not exactly planar. A very strong N—H...O hydrogen bond between two molecules related by a center produces dimer-like units separated by normal von der Waals forces.

Introduction. Crystals of *N*-carbomethoxyamino-3,6-dimethyl-4,5-diphenyl-2-pyridone (I) were supplied by Professor D. Mackay, University of Waterloo.



Preliminary precession photographs indicated the space groups *Cc* or *C*2/*c*. Intensity statistics favored *C*2/*c*, and the choice was confirmed by the structure

References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). N.R.C. Crystallographic Programs for the IBM/360 System. *World List of Crystallographic Programs*, 2nd ed., Appendix, p. 52. Utrecht: Oosthoek.
- BÜRGI, H. B. & DUNITZ, J. D. (1971). *Acta Cryst.* A27, 117–119.
- CAREY, P. R. & SCHNEIDER, H. (1974). *Biochem. Biophys. Res. Commun.* 57, 831–837.
- CAREY, P. R. & SCHNEIDER, H. (1975). *J. Amer. Chem. Soc.* In the press.
- DONOHUE, J. (1968). In *Structural Chemistry and Molecular Biology*. Edited by A. RICH and N. DAVIDSON, pp. 443–465. San Francisco: Freeman.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* 17, 1040–1044.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

analysis. A crystal 0.30 × 0.22 × 0.19 mm was mounted on a Syntex PI diffractometer and used to determine the cell constants and the intensity measurements. The experimental details were identical with those given by Dymock & Palenik (1974). Of the 2397 reflections measured, the 1927 reflections with *I* ≥ 2.0 σ(*I*) were used in the analysis. The intensities were reduced to a set of structure amplitudes on an arbitrary scale by the application of Lorentz-polarization corrections.

The structure was solved by the symbolic addition procedure using the computer programs *FAME-MAGIC-LINK-SYMP* described by Dewar (1970). The refinement was carried out by full-matrix least-squares techniques using first isotropic and then anisotropic thermal parameters. All the hydrogen atoms were located in a difference Fourier synthesis. The hydrogen atom parameters were also refined in subsequent least-squares calculations using a block approximation. The final *R* (the usual residual) was 0.040 for the 1927 reflections used in the analysis.* The final parameters are given in Tables 1 and 2.

* Tables of observed and calculated structure factors and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30999 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The quantity minimized in the calculations was $\sum w(|F_o| - |F_c|)^2$, where $w = F_o^2/a^2$ if $|F_o| < a$, $w = 1$ if $a \leq |F_o| \leq b$ and $w = b^2/F_o^2$ if $|F_o| > b$, where $a = 20.8$ and $b = 41.6$. The scattering factors for O, N and C were taken from Hanson, Herman, Lea & Skillman (1964) and for H from Stewart, Davidson & Simpson (1965).

Discussion. The aim of this structure determination was the identification of an unusual isomerization product

whose structure could not be unambiguously assigned by chemical methods. A preliminary report of the pertinent reactions and other chemical data have been given by Mackay & Wong (1974). An ORTEP drawing of the molecule and the atomic numbering is given in Fig. 1. The bond lengths are given in Table 3. Although the C(3)–C(4) and C(5)–C(6) bond distances [1.368 (3) and 1.362 (3) Å respectively] are close to the values for a double bond, the other bond lengths in-

Table 1. *The final parameters of the non-hydrogen atoms in NAPD*

All values are $\times 10^4$ except z and β_{33} , which are $\times 10^6$. The estimated standard deviations are given in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	2160 (1)	2272 (3)	6870 (4)	42 (1)	241 (5)	67 (1)	44 (3)	3 (1)	14 (1)
C(2)	3002 (1)	2278 (3)	6222 (5)	46 (1)	192 (6)	70 (2)	20 (4)	5 (1)	0 (2)
C(3)	3517 (1)	1104 (3)	8815 (5)	39 (1)	233 (6)	75 (2)	21 (4)	4 (1)	7 (2)
C(4)	3175 (1)	141 (3)	11806 (5)	41 (1)	192 (6)	66 (2)	18 (4)	0 (1)	3 (2)
C(5)	2320 (1)	372 (3)	12548 (5)	40 (1)	224 (6)	66 (2)	26 (4)	3 (1)	12 (2)
C(6)	1812 (1)	1409 (3)	10023 (5)	44 (1)	246 (6)	68 (2)	37 (4)	6 (1)	9 (2)
N(2)	1632 (1)	3226 (3)	4106 (4)	50 (1)	214 (5)	69 (1)	52 (4)	-1 (1)	15 (1)
C(7)	1631 (1)	5232 (3)	4329 (6)	54 (1)	255 (7)	89 (2)	45 (5)	1 (1)	10 (2)
O(1)	1846 (1)	6184 (3)	7096 (5)	92 (1)	288 (5)	121 (2)	64 (4)	-10 (1)	-26 (2)
O(2)	1306 (1)	5920 (2)	960 (4)	86 (1)	232 (4)	116 (2)	49 (4)	-10 (1)	30 (1)
C(8)	1222 (2)	8031 (4)	676 (10)	130 (3)	238 (8)	247 (5)	59 (8)	-24 (2)	57 (3)
O(3)	3252 (1)	3232 (2)	3439 (4)	55 (1)	242 (4)	77 (1)	2 (3)	9 (0)	22 (1)
C(22)	4417 (1)	973 (4)	7950 (7)	41 (1)	444 (9)	114 (2)	23 (5)	8 (1)	46 (3)
C(9)	3680 (1)	-1278 (3)	14269 (5)	38 (1)	238 (6)	70 (2)	19 (4)	4 (1)	15 (2)
C(10)	4212 (2)	-689 (4)	17315 (6)	64 (1)	307 (7)	89 (2)	1 (5)	-7 (1)	11 (2)
C(11)	4658 (2)	-2076 (5)	19534 (7)	60 (1)	483 (10)	95 (2)	3 (6)	-12 (1)	36 (3)
C(12)	4567 (2)	-4014 (4)	18763 (7)	50 (1)	400 (9)	133 (3)	53 (5)	7 (1)	71 (3)
C(13)	4048 (2)	-4603 (4)	15759 (8)	64 (1)	279 (8)	171 (3)	62 (6)	-3 (1)	34 (3)
C(14)	3609 (2)	-3244 (4)	13511 (7)	55 (1)	241 (6)	130 (3)	24 (5)	-10 (1)	11 (2)
C(15)	1988 (1)	-481 (3)	16152 (6)	38 (1)	290 (7)	71 (2)	42 (4)	4 (1)	20 (2)
C(16)	1649 (2)	-2316 (4)	16181 (7)	71 (2)	329 (8)	113 (2)	-7 (6)	16 (1)	24 (2)
C(17)	1375 (2)	-3098 (5)	19620 (8)	75 (2)	439 (10)	166 (3)	1 (7)	20 (1)	69 (3)
C(18)	1443 (2)	-2012 (6)	22949 (7)	60 (1)	710 (13)	108 (3)	76 (7)	13 (1)	90 (3)
C(19)	1775 (2)	-191 (5)	22957 (7)	66 (2)	689 (13)	80 (2)	-6 (8)	8 (1)	12 (3)
C(20)	2049 (2)	580 (5)	19554 (6)	59 (1)	474 (9)	75 (2)	-8 (6)	8 (1)	4 (2)
C(21)	907 (2)	1693 (4)	10406 (7)	45 (1)	497 (10)	108 (2)	97 (6)	10 (1)	51 (3)

Table 2. *The final parameters of the hydrogen atoms in NAPD*

The atom is given followed by the positional parameters ($\times 10^3$), the isotropic temperature factor and the distance (Å) to the atom to which it is bonded. The estimated standard deviations are in parentheses.

	x	y	z	B (Å ²)	Distance	to atom
H(1)	163 (1)	267 (3)	15 (1)	6.2 (0.6)	0.97 (2)	N(2)
H(2)	122 (3)	835 (6)	-21 (1)	15.9 (1.2)	0.99 (4)	C(8)
H(3)	160 (2)	866 (6)	22 (1)	15.0 (1.2)	0.89 (4)	C(8)
H(4)	68 (3)	818 (6)	5 (1)	16.2 (1.2)	0.88 (4)	C(8)
H(5)	452 (2)	82 (4)	54 (1)	9.9 (0.8)	0.92 (3)	C(22)
H(6)	478 (2)	43 (4)	99 (1)	8.8 (0.7)	0.94 (3)	C(22)
H(7)	465 (2)	223 (4)	79 (1)	11.3 (0.9)	0.94 (3)	C(22)
H(8)	428 (1)	69 (3)	178 (1)	6.1 (0.6)	0.97 (2)	C(10)
H(9)	507 (2)	-164 (4)	215 (1)	9.3 (0.7)	0.98 (3)	C(11)
H(10)	489 (2)	-502 (4)	204 (1)	7.9 (0.7)	1.02 (2)	C(12)
H(11)	398 (2)	-605 (4)	151 (1)	10.8 (0.8)	1.03 (3)	C(13)
H(12)	324 (1)	-361 (3)	114 (1)	7.3 (0.6)	0.95 (3)	C(14)
H(13)	158 (1)	-308 (4)	137 (1)	7.3 (0.6)	1.01 (2)	C(16)
H(14)	114 (2)	-441 (4)	192 (1)	9.8 (0.8)	0.98 (3)	C(17)
H(15)	128 (2)	-251 (4)	254 (1)	9.4 (0.8)	0.97 (3)	C(18)
H(16)	177 (2)	81 (4)	253 (1)	10.6 (0.8)	1.05 (3)	C(19)
H(17)	229 (2)	201 (4)	195 (1)	9.3 (0.7)	1.06 (3)	C(20)
H(18)	56 (2)	140 (4)	81 (1)	8.4 (0.7)	0.98 (2)	C(21)
H(19)	72 (2)	114 (4)	127 (1)	8.3 (0.7)	0.93 (2)	C(21)
H(20)	80 (2)	307 (4)	106 (1)	9.1 (0.7)	0.96 (3)	C(21)

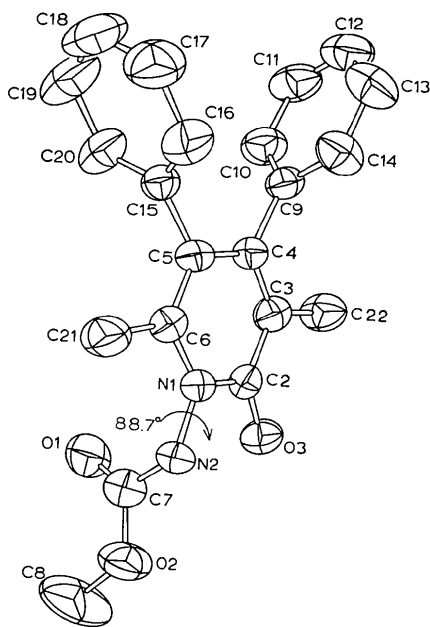


Fig. 1. An ORTEP drawing of the *N*-carbomethoxyamino-3,6-dimethyl-4,5-diphenyl-2-pyridone molecule showing the atomic numbering and thermal ellipsoids. The hydrogen atoms are not shown for clarity. The molecules are linked *via* a hydrogen bond involving H(1) on N(2) and O(3) of a molecule related by a center of symmetry. The dihedral angle between the plane N(1) to C(6) and the N(2), C(7), O(1), and O(2) plane is also shown.

indicate extensive delocalization in the pyridone ring. A summary of the bond distances and a discussion of the π -delocalization in 2-pyridones have been given by Wheeler & Ammon (1974). The distances in (I) tend to be larger [except for N(1)–C(2) and C(2)–C(3)] than in the other 2-pyridone derivatives; this may be caused by overcrowding because of the number of substituents on the ring. Alternatively, the aromaticity index A [see Wheeler & Ammon (1974) for definitions and references] is 0.83 for (I) compared with 1.0 for pyridine and 0.72 for the 2-pyridone studied by Wheeler & Ammon (1974), suggesting an increase in the π -delocalization. The pyridone ring is only approximately planar with the largest deviation from the six-atom plane being 0.041 Å. The two methyl groups C(22) and C(21) are in the plane (deviations of -0.025 and $+0.024$ Å respectively) although the other substituents are definitely out of the plane of the ring [O(3) is $+0.089$, C(9) is -0.233 , C(15) is $+0.175$ and N(2) is -0.166 Å]. The

planes of the phenyl rings and the carbomethoxyamino group are almost perpendicular to the pyridone ring with dihedral angles of 79.1° for plane C(9) to C(14), 86.4° for plane C(15) to C(20) and 88.7° for the plane containing N(2), C(7), O(1) and O(2).

Table 3. Bond distances (Å)

N(1)–C(2)	1.389 (3)	C(4)–C(9)	1.500 (3)
N(1)–C(6)	1.386 (3)	C(9)–C(10)	1.380 (3)
C(2)–C(3)	1.432 (3)	C(10)–C(11)	1.393 (4)
C(3)–C(4)	1.368 (3)	C(11)–C(12)	1.357 (4)
C(4)–C(5)	1.425 (3)	C(12)–C(13)	1.359 (4)
C(5)–C(6)	1.362 (3)	C(13)–C(14)	1.378 (4)
N(1)–N(2)	1.404 (2)	C(14)–C(9)	1.373 (3)
N(2)–C(7)	1.373 (3)	C(5)–C(15)	1.502 (3)
C(7)–O(1)	1.192 (3)	C(15)–C(16)	1.368 (4)
C(7)–O(2)	1.335 (3)	C(16)–C(17)	1.398 (4)
O(2)–C(8)	1.452 (3)	C(17)–C(18)	1.368 (4)
C(2)–O(3)	1.248 (2)	C(18)–C(19)	1.355 (5)
C(3)–C(22)	1.502 (3)	C(19)–C(20)	1.384 (4)
C(6)–C(21)	1.485 (3)	C(20)–C(15)	1.380 (3)

A strong intermolecular hydrogen bond links two molecules related by a center of symmetry into a dimer-like unit. The intermolecular contacts between the dimer-like units are the usual van der Waals forces. The dimensions of the hydrogen bond [N(2)···O(3') 2.807 (2) Å, H(1)···O(3') 1.84 (2) Å, and the N(2)–H(1)···O(3') 173 (2)°] are indicative of a strong N–H···O type hydrogen bond.

We wish to thank the Department of Chemistry for a Postdoctoral Fellowship (to M.M.) and the Northeast Regional Data Center at the University of Florida for a grant of computer time.

References

- DEWAR, R. B. K. (1970). *Crystallographic Computing*, edited by F. R. AHMED, pp. 63–65. Copenhagen: Munksgaard.
- DYMOCK, K. & PALENIK, G. J. (1974). *Acta Cryst.* **B30**, 1364–1366.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
- MACKAY, D. & WONG, L. L. (1974). *Chem. Commun.* pp. 621–622.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–2187.
- WHEELER, G. L. & AMMON, H. L. (1974). *Acta Cryst.* **B30**, 680–687.