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The Crystal Structure of 2-Acetylcyclopentadienone-1-phenylhydrazone

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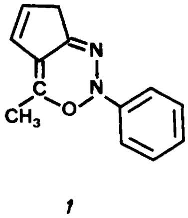
The structure of 2-acetylcyclopentadienone-1-phenylhydrazone, $C_{13}H_{12}N_2O$, has been determined by X-ray diffraction. The red crystals are triclinic with unit cell parameters $a=8.424(2)$, $b=8.719(2)$, $c=15.875(3)$ Å, $\alpha=85.24(2)$, $\beta=86.22(2)$, $\gamma=68.81(2)°$, $Z=4$, and the space group is $P\bar{1}$. Based on 1660 observed reflections measured at −135 °C, the structure was refined to a final R-value of 0.077.

There are two crystallographically independent, but quite similar molecules in the asymmetric unit. They have the typical hydrazone form with hydrogen bonded to nitrogen. The molecules consist of a methyl group and three roughly planar rings: a phenyl ring, a cydopentadienyl ring and a seven-membered $\overline{C{-}O\cdots H{-}N{-}N{-}C{-}C}$ ring held together by a strong hydrogen bond between the acetyl oxygen and hydrazone hydrogen atom. Except for the methyl hydrogens, the molecules are nearly planar, and all interplanar angles between the rings are less than 8°.

During a study of the reaction between 1,1-diacetylferrocene and aryldiazonium salts, products of the type $C_7H_7N_2O-Ar$ were reported.[1,2] The product (Ar=phenyl) was first believed to be the isomers of 2-phenyl-1,2,3-oxadiazine[1] with structures *1–3*.

The main reasons for these assignments included negative evidence for the presence of keto and enol groups.[1] A later study concluded that only two other structures were possible, namely *4* nad *5*, and that *4* was the more plausible one.[2] The reasoning was based on ^1H NMR, IR and UV data plus solubility behaviour, all pointing to *4* as the probable structure. In order to distinguish between these structures, it was decided to solve the structure using X-ray crystallography.



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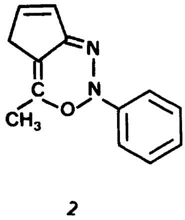

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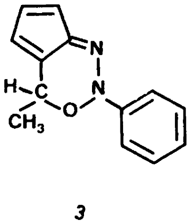

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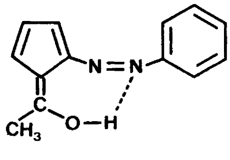

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EXPERIMENTAL

The preparation, elemental analysis and some spectra of the compound have been reported elsewhere.[2] Intensity data and data for determination of unit cell parameters were obtained on an Enraf-Nonius CAD 4 diffractometer at −135 °C.

Unit cell parameters were based on least-squares refinement of the setting angles of 25 general reflections with 2θ between 10 and 24°. They are a=8.424(2) Å, b=8.719(2) Å, c=15.875(3) Å, α=85.24(2), β=86.22(2), γ=68.81(2)°, d_x=1.302 g/cm^3, Z=4 and $\mu(\mathrm{Mo}K\alpha)$=0.788 cm^{-1}. The red crystals are triclinic, the possible space groups being $P1$ or $P\bar{1}$ (No. 1 or 2).

Reflection intensities were collected using an omega scan and graphite monochromated Mo$K\alpha$ radiation (λ=0.71073 Å). The scan width was set to (1.00+0.35 tg θ)° and the scan rate was kept constant at 2°/min. From a total of 3373 unique reflections with $2\theta \leqslant 48°$, 1660 had $I \geqslant 2\sigma(I)$ and were classified as observed. Less than half of the measured reflections were

Table 1. Final atomic parameters with standard deviations.

Atom	x	y	z	B
Molecule I				
O1	0.0259(5)	0.2893(4)	0.8874(2)	2.11(8)
N101	0.3059(5)	0.3664(5)	0.9972(3)	1.67(9)
N102	0.2588(5)	0.2388(5)	1.0016(3)	1.56(9)
C101	−0.1358(7)	0.5099(7)	0.7958(4)	2.1(1)
C102	−0.0000(7)	0.4342(6)	0.8594(4)	1.9(1)
C103	0.0912(6)	0.5330(6)	0.8846(4)	1.6(1)
C104	0.0640(7)	0.6930(6)	0.8523(4)	1.7(1)
C105	0.1793(7)	0.7536(7)	0.8861(4)	1.9(1)
C106	0.2805(7)	0.6340(7)	0.9408(4)	1.9(1)
C107	0.2294(7)	0.4945(6)	0.9433(4)	1.7(1)
C108	0.3274(6)	0.1062(6)	1.0616(3)	1.4(1)
C109	0.2659(7)	−0.0228(6)	1.0651(4)	1.8(1)
C110	0.3281(7)	−0.15404(7)	1.1224(4)	2.1(1)
C111	0.4480(7)	−0.1591(7)	1.1782(4)	2.4(1)
C112)	−0.5068(7)	−0.0307(7)	1.1752(4)	2.4(1)
C113	0.4491(7)	0.1031(6)	1.1170(4)	1.7(1)
H102	0.170(6)	0.231(5)	0.970(3)	2
Molecule II				
O2	0.2446(5)	−0.526(4)	0.6047(2)	2.25(8)
N201	0.1322(5)	−0.2989(5)	0.4942(3)	1.82(9)
N202	0.2719(5)	−0.2625(5)	0.4867(3)	1.50(9)
C201	0.0343(7)	0.1020(7)	0.7006(4)	2.1(1)
C202	0.0983(7)	−0.0220(7)	0.6353(4)	2.0(1)
C203	−0.0129(6)	−0.1015(6)	0.6116(4)	1.5(1)
C204	−0.1730(7)	−0.0736(7)	0.6469(4)	2.3(1)
C205	−0.2516(7)	−0.1740(7)	0.6100(4)	2.2(1)
C206	−0.1384(7)	−0.2666(7)	0.5532(4)	2.0(1)
C207	0.0116(7)	−0.2266(7)	0.5492(4)	1.8(1)
C208	0.4035(6)	−0.3420(6)	0.4287(3)	1.5(1)
C209	0.5456(7)	−0.2950(6)	0.4224(4)	1.8(1)
C201	0.6814(7)	−0.3764(7)	0.3697(4)	2.1(1)
C211	0.6775(7)	−0.4993(7)	0.3242(4)	2.1(1)
C212	0.5349(7)	−0.5447(7)	0.3284(4)	2.1(1)
C213	0.3962(7)	−0.4660(7)	0.3806(4)	1.9(1)
H202	0.292(6)	−0.181(5)	0.526(3)	2

observed. This is due to the very small size of the crystals. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Data collection- and computer programs used in this work belong to the Enraf-Nonius Structure Determination Pack, SPD-Plus 1982. The reader is referred to a previous paper for further details.[3]

STRUCTURE DETERMINATION

The structure was solved by means of direct methods (MULTAN), and refined by full-matrix least-squares iterations assuming the correct space group to be $P\bar{1}$. Subsequent successful refinement justified the choice of space group.

There are two crystallographically independent molecules in the asymmetric unit. Thus a very large number of parameters have to be refined. Due to the limited number of reflections, isotropic temperature factors were used for all atoms.

Most hydrogen positions, including those of both H102 and H202 involved in hydrogen bonding, were found from difference maps. The other hydrogen atoms were placed geometrically. All hydrogens were given a common constant temperature factor (B=2.0), but their positional parameters were refined.

The function minimized is $\sum w(\Delta F)^2$, attributed weights correspond to counting statistics plus 2 % of the net intensity (p factor=0.02).[3] The refinement converged at R=0.077, R_w=0.055 and S=1.502.

A final difference map showed no peaks above 0.4e/Å^3. Refined atomic parameters for the non-hydrogen atoms plus H102 and H202 are listed in Table 1. Final bond lengths and

Table 2. Bond distances (Å) in the molecules.

	Molecule (i=1)	Molecule (i=2)
Ci01–Ci02	1.504(7)	1.492(7)
Ci02–Ci03	1.439(6)	1.435(6)
Ci03–Ci04	1.389(6)	1.370(7)
Ci04–Ci05	1.413(7)	1.450(7)
Ci05–Ci06	1.368(7)	1.351(7)
Ci06–Ci07	1.427(7)	1.423(7)
Ci07–Ci03	1.465(6)	1.485(7)
Ci07–Ni01	1.337(6)	1.305(6)
Ni01–Ni02	1.305(5)	1.321(5)
Ni02–Ci08	1.410(6)	1.404(6)
Ci08–Ci09	1.395(7)	1.394(6)
Ci09–Ci10	1.366(7)	1.378(7)
Ci10–Ci11	1.374(7)	1.352(7)
Ci11–Ci12	1.374(7)	1.390(7)
Ci12–Ci13	1.387(7)	1.382(7)
Ci13–Ci08	1.385(6)	1.396(6)
Ci02–Oi	1.249(5)	1.237(5)
Ni02–Hi02	0.96(4)	1.04(5)
Hi02...Oi	1.76(4)	1.68(4)
Ni02...Oi	2.654(5)	2.668(5)
Csp^2–H(average)	0.96(5)	
C_{Me}–H(average	1.01(4)	

Table 3. Bond angles (°) in the molecules.

	Molecule I (i=1)	Molecule II (i=2)
Ci01−Ci02−Ci03	118.1(5)	118.1(5)
Ci01−Ci02−Oi	117.8(5)	118.7(5)
Ci03−Ci02−Oi	124.1(5)	123.1(5)
Ci02−Ci03−Ci04	123.9(4)	124.0(5)
Ci02−Ci03−Ci07	131.0(5)	131.1(5)
Ci04−Ci03−Ci07	105.1(4)	104.9(4)
Ci03−Ci04−Ci05	110.4(5)	110.5(5)
Ci04−Ci05−Ci06	108.7(5)	107.9(5)
Ci05−Ci06−Ci07	108.2(5)	109.2(5)
Ci06−Ci07−Ci03	107.7(5)	107.5(5)
Ci06−Ci07−Ni01	117.9(5)	117.6(5)
Ci03−Ci07−Ni01	134.3(5)	134.9(5)
Ci07−Ni01−Ni02	118.9(4)	119.7(4)
Ni01−Ni02−Ci08	120.7(4)	120.1(4)
Ni01−Ni02−Hi02	125(3)	122(2)
Ci08−Ni02−Hi02	114(3)	118(2)
Ni02−Ci08−Ci09	117.6(4)	117.2(5)
Ni02−Ci08−Ci13	122.1(5)	122.0(5)
Ci09−Ci08−Ci13	120.2(5)	120.7(5)
Ci08−Ci09−Ci10	119.8(5)	118.9(5)
Ci09−Ci10−Ci11	120.9(5)	120.9(5)
Ci10−Ci11−Ci12	119.1(6)	120.7(5)
Ci11−Ci12−Ci13	121.8(5)	120.1(5)
Ci12−Ci13−Ci08	118.2(5)	118.6(5)
Ci02−Oi...Hi02	111(2)	113(2)
Ni02−Hi02...Oi	154(4)	156(4)

Table 4. Interplanar and torsional angles in the molecules.[a]

No. of plane	Atoms included	Interplanar angles (°)	i=1	i=2
		1i/2i	2.5	1.8
1i	Oi, Ci01, Ci02, Ci03	1i/3i	8.8	5.3
2i	Ci03, Ci04, Ci05, Ci06, Ci07	1i/4i	3.0	3.3
3i	Ci08, Ci09, Ci10, Ci11, Ci12, Ci13	2i/3i	8.0	4.5
4i	Oi, Ci02, Ci03, Ci07, Ni01, Ni02	2i/4i	3.4	2.3
		3i/4i	5.8	6.5

Torsional angles					
Ci07	Ni01	Ni02	Ci08	−175.6	178.8
Ci07	Ni01	Ni02	Hi02	−2.0	2.9
Ni02	Ni01	Ci07	Ci03	2.3	0.3
Ni02	Ni01	Ci07	Ci06	178.8	178.3
Ni01	Ni02	Ci08	Ci09	177.3	178.4
Ni01	Ni02	Ci08	Ci13	−1.4	−3.2
Oi	Ci02	Ci03	Ci04	178.9	177.6
Oi	Ci02	Ci03	Ci07	1.3	−1.4

[a] H102 is −0.200 Å from plane 11 and −0.094 Å from plane 41. H202 is 0.150 Å from plane 12 and 0.032 Å from plane 42.

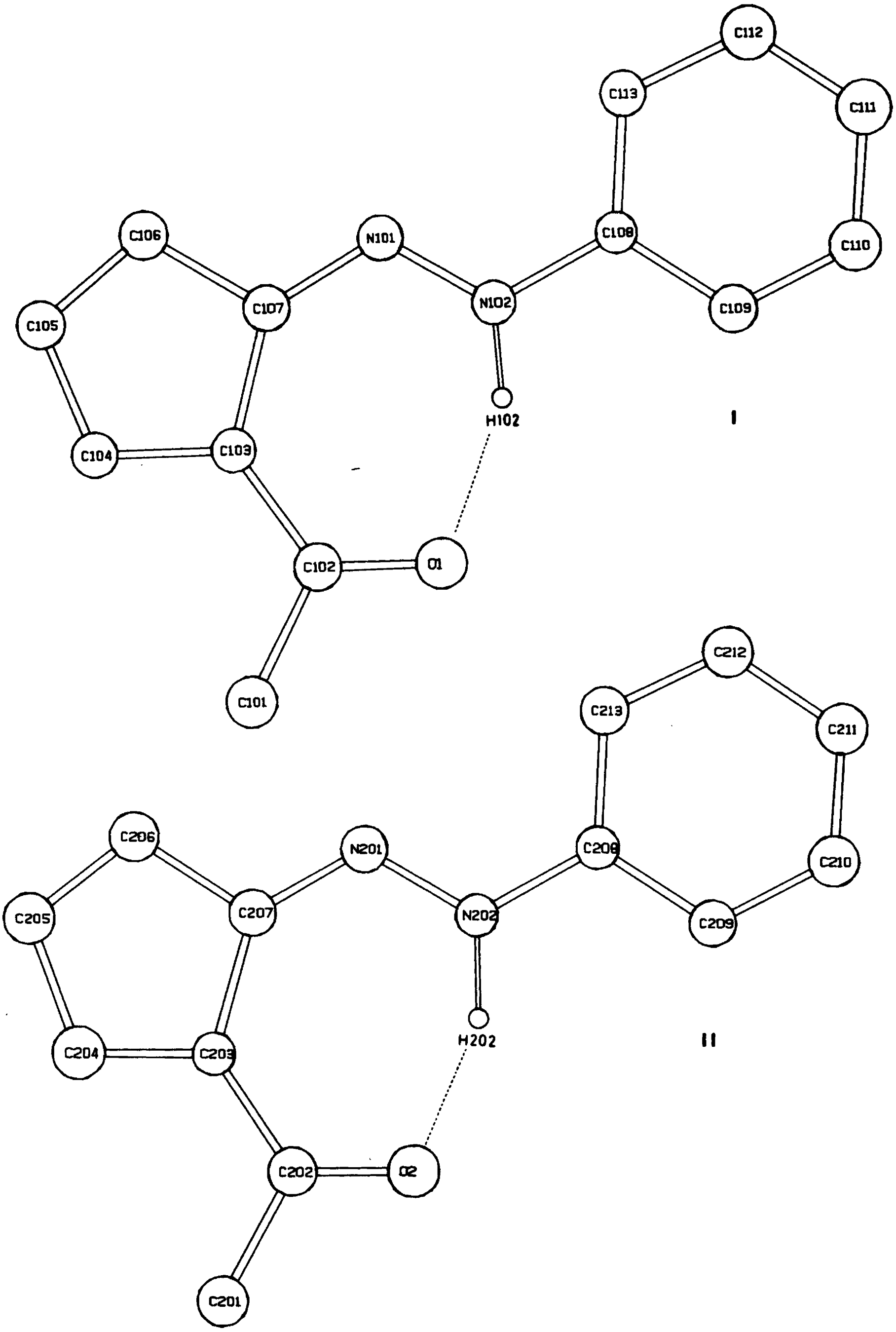


Fig. 1. The two crystallographically independent molecules as seen along the normals to the planes through O1, N102, C107(I) and O2, N202, C207(II).

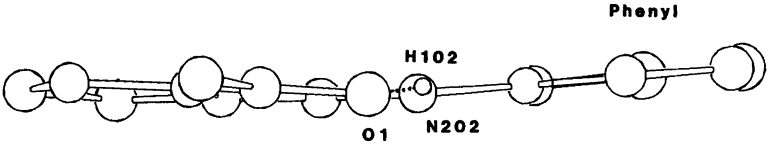
angles are listed in Tables 2 and 3, while interplanar and torsional angles are listed in Table 4. Positional parameters for the hydrogen atoms, as well as observed and calculated structure factors are available from the authors S.H. and K.M.M. upon request.

RESULTS AND DISCUSSION

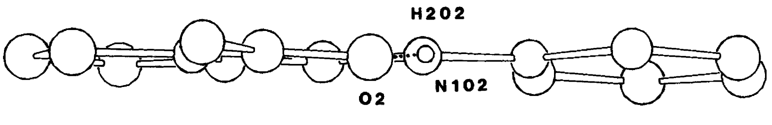
Molecular geometry. There are two very similar, but crystallographically independent molecules in the asymmetric unit. Their structures clearly identify them as molecules of 2-acetylcyclopentadienone-1-phenylhydrazone. From Figs. 1 and 2 and from Table 4, it can be seen that the molecules are nearly planar, although molecule I is slightly bent at N102 and therefore less planar than molecule II. The acetyl, cyclopentadienyl and phenyl groups are essentially planar; all atoms of a group are within 0.012 Å of the best plane through that group. The cyclopentadienyl and the phenyl groups are positioned *trans* with respect to the N−N bond, thus permitting close contact between the hydrogen atom bonded to nitrogen and the acetyl oxygen atom. As a result of this, an internal hydrogen bond is formed between these two atoms in both molecules.

Molecular bonding and conjugation. The bonding clearly identifies the molecules as the hydrazones, *5*, and not as the tautomeric azo compounds, *4*. In *5* one would expect an atomic bonding sequence O1=C102−C103−C107=N101−N102(H)−C(Ph). In *4* one would expect the sequence (H)O1−C102=C103−C107−N101=N102−C(Ph). The sequences listed above are for molecule I, the corresponding ones would be expected for molecule II.

For C102−O1/C202−O2 the bond lengths found are 1.249(5) and 1.237(5) Å. This is slightly longer than a normal C−O double bond length and may be compared to the sum of Paulings covalent double bond radii (1.22 Å),[4] and 1.23(1) Å, the value given for the C−O double bond length in ketones, aldehydes etc.[5] Similar bond lengths as these found in the



Molecule I



Molecule II

Fig. 2. The molecules seen at right angles to the normals of Fig. 1.

present investigation are also found for such bonds in other hydrazones.[18,19] An azo (or enol) form of the molecules would be expected to have a C−O(H) single bond length of 1.43(1) Å.[4,5]

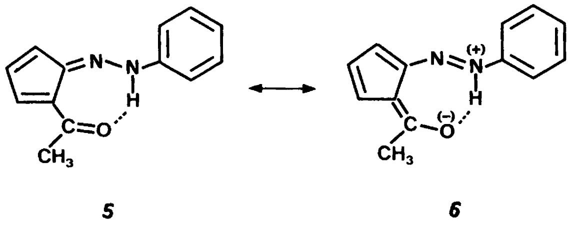
The C102−C103/C202−C203 bond lengths are 1.439(6) and 1.435(6) Å, slightly shorter than 1.48 Å which is twice the single bond radius of sp^2 hybridized carbon.[20] For C103−C107/C203−C207 the bond lengths are 1.465(6) and 1.485(7) Å, corresponding to a single bond between two sp^2 hybridized carbons. The C107−N101/C207−N201 bond lengths are 1.337(6) and 1.305(6) Å, comparable to the C−N partial double bonds found in dialkyldithiocarbamate compounds and somewhat longer than the corresponding double bond near 1.27 Å found in oximes.[6,21] They are, however, close to corresponding bond lengths found in other hydrazones (1.27−1.34 Å).[6–9,11–19,22–30] For the N101−N102/N201−N202 bond lengths, values of 1.305(5) and 1.321(5) Å are found. They are comparable to corresponding bond lengths found in other hydrazones with internal N−H···O=C bonds, [6–9,11,13–19] but significantly shorter than an N−N single bond of 1.40 Å.[4] Lengths of N−N double bonds are found closer to 1.24 Å.[5,31–34] From the above, we conclude that the compound is a true hydrazone and that the conclusion holds even if the hydrogen position had not been found.

There is no clear-cut sequence of pure single and double bonds in the hydrazone C−N−N(H)-groups; the bonds are both partial double bonds, but this is common for hydrazones.

Looking at the molecules and the bond lengths, we see that there is a tendency to conjugation starting with the N−N bond, continuing through the cyclopentadienyl group and ending in the C−O group. The sequence of double and single bonds is best outlined in *5*. (The phenyl groups with N−C(Ph) bond lengths averaging 1.407 Å, as compared to a N−Csp^2 single bond of 1.44 Å,[4,5] may also be considered weakly conjugated to the above system). Except perhaps for the C−O bond, the bonds in the conjugated system are not pure single or double bonds. This may be expressed by the resonance *5*↔*6*.

Inspection of Table 2 shows that form *5* dominate and more so in molecule II than in molecule I. In agreement with the above, all atoms, except for the hydrogens and the methyl carbon atom, are sp^2 hybridized as can be seen from the bond angles in Table 3. Recent work by Vickery, Drew and Willey on phenylhydrazones show similar conjugation and bonding. For systems with strong intramolecular bonding, they find average bond lengths of 1.313, 1.307 and 1.400 Å for the C−N(H)−N−C sequence (averages in the present investigation are 1.321, 1.313 and 1.407 Å). Without such hydrogen bonds, the corresponding average bond lengths are 1.28, 1.39 and 1.36 Å.[18,19]

Hydrogen bonding. An intramolecular hydrogen bond is formed between the acetyl oxygen and N−H in both molecules I and II. This hydrogen bond locks the molecules in a near planar form and forms a seven-membered ring which is planar within 0.07 Å. Due to the planarity, the ring is strained as manifested in the large angles C102−C103−C107/



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C202–C203–C207 being 131.0(5)/131.1(5)° and C103–C107–N101/C203–C207–N201 being 134.3(5)/134.9(5)°. In a series of azo dyes and other phenylhydrazones, similar hydrogen bonding – mostly forming 6-rings – also locks the molecules into a stable, planar conformation.[6–9,11–19] In fact the bright red hydrazone in the present investigation may itself be considered an azo dye. The C=O···H–N hydrogen bonds have the following lengths; O···N=2.654(5) and 2.668(5) Å, O···H=1.76(4) and 1.68(4) Å, H–N=0.96(4) and 1.04(5) Å for molecules I and II, respectively. These values correspond well to those found by Vickery, Drew and Willey for a series of phenylhydrazones with intramolecular hydrogen bonds forming 6-rings (typical value 2.65 Å),[19] and to an internal P=O···H–N bond (6-ring) in methyl phenyl[*syn*-*α*-(tosylhydrazono)benzyl]-phosphinate.[30] According to a recent survey by Emsley *et al*,[35] they represent strong hydrogen bonds. The strength of the bonds is partly due to the resonance mentioned above. It leads to a shift of electron density from the N–H nitrogen to the carbonyl oxygen, thereby enhancing the hydrogen bond donor and acceptor properties of the respective groups.

In another survey, Taylor and Kennard, by comparison of X-ray and neutron diffraction results for 57 C=O···H–N bonds (determined by both methods), found that the X-ray values for N–H and H···O distances show an average systematic shift of ≈0.1 Å (N–H too short, H···O too long).[36]

The N–H···O angles found in the present work have an average value of 155(1.5)° while the corresponding value for C–O···H is 112(1.5)°. Thus the latter value shows that the hydrogen bonding occurs nearly in the direction of one of the two sp^2 lone pairs of electrons on oxygen. This is normal for such bonds.[37]

The IR spectrum of 2-acetylcyclopentadienone-1-phenylhydrazone shows a broad absorption near 2690 cm^{-1}. This was originally assigned to O–H stretching (with the OH-group involved in hydrogen bonding according to structure *4*).[2] This seemed to be corroborated by the ^{1}H NMR spectrum where a presumed hydroxyl hydrogen signal was found in CCl_4 at 15.05 ppm.[2] The IR spectrum at wave numbers above 1650 cm^{-1} and the NMR spectrum were run in solution. Although it is perhaps unlikely, it is not impossible that

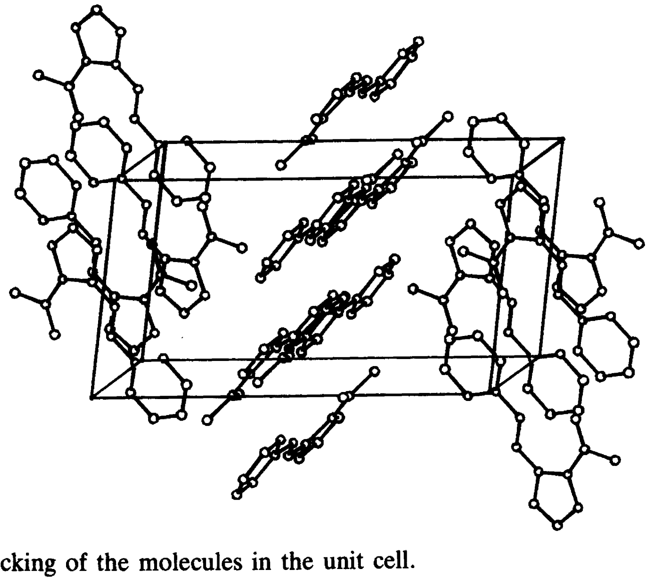

Fig. 3. The packing of the molecules in the unit cell.

at least some molecules exist in the azo(enol) form in solution. Such equilibria are known to exist.[38–40] However, the spectra may also be compatible with a strongly hydrogen-bonded NH group in a conjugated system. In tetraphenyldithioimidodiphosphinic acid, its tetramethyl analog and the thioxo analog, ν(N–H) was found near 2620, 2610 and 2690 cm^{-1}, respectively.[41,42] In the first compound the NH group has been shown to be hydrogen bonded to a sulfur atom.[41] Similar hydrogen bonding probably exists in the two other compounds (to oxygen in the second).

From more recent work on phenylhydrazones, and also in certain other systems with C=O···NH bonds, ^{1}H NMR data show that the NH proton signal may occur at lower fields than 15 ppm.[17,18,43]

The IR spectrum (below 1650 cm^{-1} of the solid in KBr) showed no ν(C=O) absorption above 1600 cm^{-1}. Since the C=O group is part of a conjugated system and in addition hydrogen bonded, it is expected to absorb at a very low frequency.[44] The strengthening of the hydrogen bond by shift of charge from nitrogen to oxygen (see resonance form *6* above), should further lower the ν(C=O) absorption frequency. Thus, assuming no structural change in going from the crystalline solid to the KBr mull, this absorption probably occurs in the region just below 1600 cm^{-1}.[2] A corresponding absorption is found for $CH_3CH_2CH_2C(O)NHNHC(O)CH_2CH_2CH_3$ in the same region.[45] Also the fact that the observed C=O bond lengths appear to be slightly longer than expected for a double bond, is in agreement with the above.

Molecular packing. There are no hydrogen bonds between the molecules. From Fig. 3 it can be seen that the molecules are stacked parallel to each other. The stacks are inclined relative to each other resulting in a herringbone pattern.

There are several intermolecular contacts shorter than normal van der Waals contacts (typical values are C···C=3.4–3.6 Å and C···N=3.3–3.4 Å).

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