β-Diketone Interactions. Part 1. Pentane-2,4-dione–Diethylamine Adduct. X-Ray Structure Reveals Novel Hydrogen-bonded Dimer

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When mixed, pentane-2,4-dione (PD) and diethylamine (DEA) produce unstable crystals of a 1:1 adduct which slowly condense with time to form 4-diethylaminopent-3-en-2-one. An X-ray crystal structure of the adduct shows it to be a dimer with alternate PD and DEA molecules held together by N–H ···O hydrogen bonds one of which is a three-centre hydrogen bond.

The first chemist to investigate the keto $\rightleftharpoons$ enol equilibrium of PD by [1]H n.m.r. was Reeves [1] who also reported on the effects of amines.[2] One of these, DEA, formed a molecular complex which he postulated would have structure (1) or (2). A much

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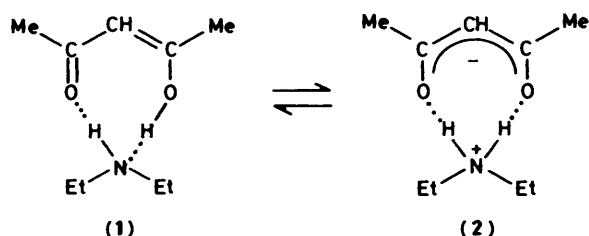
better known interaction of PD and secondary amines is the production of enaminones.[3–6] The formation of an adduct such as (1) is not postulated as an intermediate in this type of reaction, which is based on the nucleophilic attack of the amine on a carbonyl carbon.[7]

The interaction of PD with tertiary amines has also been investigated and it has been proposed that three-centre hydrogen bonds are involved (3)[8,9] or that proton transfer has occurred with the proton equally attracted to both oxygens (4).[10]

(3)　　　　　(4)
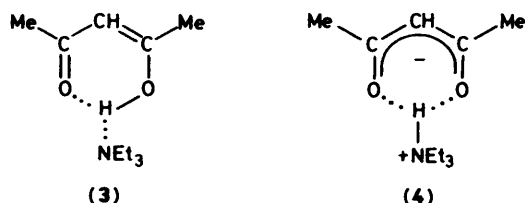
Because of the unusual type of hydrogen bonding exhibited by β-diketones such as PD[11] and their puzzling behaviour with certain amines we have reinvestigated the system PD + DEA with a view to uncovering the nature of the adduct PD·DEA.

Results and Discussion

The crystalline adduct formed between PD and DEA was thought by Reeves to have the structure (1).[1] The volatility of this adduct may have prevented its structure determination until now. However, the picture that has emerged is noteworthy in several respects: the perfectly square NHO framework of hydrogen bonds holding the four molecules together; the approximately co-planar arrangement; the three-centre hydrogen bonds, this being the first time such bonding has been
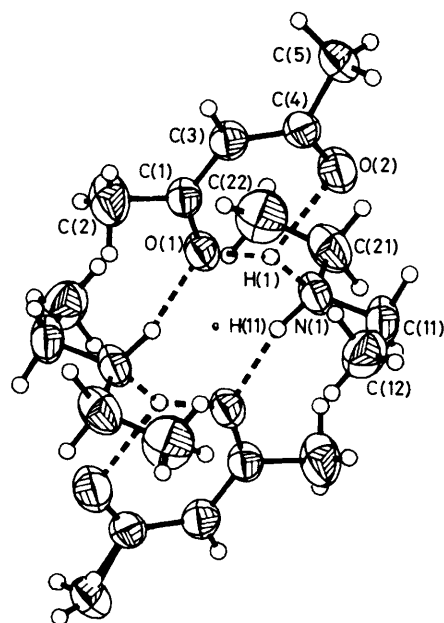
Figure 1. Structure and atom labelling of PD·DEA illustrating hydrogen bonding across centre of symmetry [18]

demonstrated for PD; and the rather atypical bond lengths and angles of PD itself.

Curiously the crystal structure of PD, the most investigated of the β-diketones, has never been determined, but in 1983 it was discovered in crystals of the drug diphenylhydantoin 9-ethyl-adenine where PD molecules were incorporated as a solvate.[12] Here the PD was present as the hydrogen bonded cis-enol tautomer with $R(O \cdots O) = 2.535$ Å, and the investigators claimed it to be free of intermolecular forces. However, the enol proton was considerably above the plane of the molecule (0.36 Å) suggesting that lattice forces were not entirely without influence.

Our structural determination again reveals PD to be in the cis-enol configuration, but here it is involved in a very different hydrogen bonding system and the increase of $R(O \cdots O)$ to 2.920 Å is a reflection of this. Significantly longer than in any other cis-enol, this value of $R(O \cdots O)$ is only a little less than the sum of the Van der Waals radii of two oxygen atoms (3.00 Å).[13] Weak though the intramolecular hydrogen bonding between these oxygens is, it is still exerting a restraining influence on the conformation of the PD molecule.
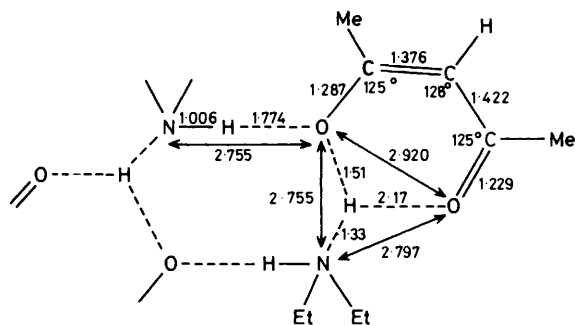
The structure of (PD·DEA)₂, Figure 1, shows the PD moiety

Figure 2. Hydrogen bonding network of (PD·DEA)₂

Table 1. Fractional atomic co-ordinates (× 10⁴) for (PD·DEA)₂

	x	y	z
C(1)	969(8)	2 494(11)	10 095(4)
C(2)	1 732(5)	1 736(7)	9 434(2)
O(1)	3 102(4)	1 055(5)	9 614(2)
C(3)	950(6)	1 798(7)	8 694(3)
C(4)	1 485(5)	1 218(7)	7 987(3)
O(2)	2 754(4)	496(6)	7 933(2)
C(5)	383(7)	1 491(9)	7 244(3)
N(1)	5 308(5)	−847(6)	8 912(2)
C(11)	6 257(7)	182(10)	8 394(3)
C(12)	6 445(8)	2 090(11)	8 652(4)
C(21)	4 849(8)	−2 662(9)	8 618(3)
C(22)	3 761(9)	−3 583(10)	9 110(5)

Table 2. Bond lengths (Å) and bond angles (°) for (PD·DEA)₂

C(2)–C(1)	1.493(9)	O(1)–C(2)	1.287(6)
C(3)–C(2)	1.376(7)	C(4)–C(3)	1.422(7)
O(2)–C(4)	1.229(6)	C(5)–C(4)	1.520(8)
C(11)–N(1)	1.490(8)	C(21)–N(1)	1.470(8)
C(12)–C(11)	1.480(10)	C(22)–C(21)	1.500(12)
N(1)–H(1)	1.330(58)	N(1)–H(11)	1.006(71)

O(1)–C(2)–C(1)	115.6(5)	C(3)–C(2)–C(1)	119.4(5)
C(3)–C(2)–O(1)	125.0(5)	C(4)–C(3)–C(2)	128.2(5)
O(2)–C(4)–C(3)	125.1(5)	C(5)–C(4)–C(3)	117.1(5)
C(5)–C(4)–O(2)	117.7(5)	C(21)–N(1)–C(11)	113.5(5)
C(12)–C(11)–N(1)	110.5(6)	C(22)–C(21)–N(1)	112.1(6)
C(11)–N(1)–H(1)	114.5(24)	C(21)–N(1)–H(1)	107.4(25)
C(11)–N(1)–H(11)	120.0(35)	C(21)–N(1)–H(11)	104.1(36)
H(1)–N(1)–H(11)	95.2(42)		

to have distinguishable C=O, C–O, C=C, and C–C bonds. Indeed the first of these, the carbonyl bond [C(4)–O(2)], at 1.229(6) Å is shorter than any other β-diketone carbonyl. The structure of nine compounds of this class have been determined to date. In all of them there is a strong OHO intramolecular hydrogen bond.[11]

The most noteworthy feature of (PD·DEA)₂ is its hydrogen bonding. The dimer is held together by an exactly square arrangement of two oxygens and two nitrogens with $R(O \cdots N)$ = 2.755 Å (Figure 3). These bonds are *ca.* 0.30 Å shorter than the sum of the Van der Waals radii (3.05 Å)[13] which makes them strong hydrogen bonds, but not the strongest NHO bonds some of which are as short as 2.600 Å in 2-hydroxyphenyl phenylphosphonate,[14] and 2.611 Å in benzotriazolium hydrogen phosphate.[15] This square planar framework of hydrogen bonds is almost co-planar with the two PD molecules (Table 4).

The most remarkable aspect of the adduct however is the pair of three-centre hydrogen bonds. The two oxygens of PD and the nitrogen of DEA form an approximately isosceles triangle (Figure 2). Within this lies the enol proton, off-centre and nearer the apex nitrogen (1.33 Å) than the base oxygen O(1) (1.51 Å). The third atom O(2), at $R(O \cdots O)$ = 2.17 Å, deomonstrates the overall asymmetry of the proton's location. In many such NHO three-centre bonds there are almost equal $R(O \cdots H)$ distances falling in the range 1.8—2.4 Å.[16]

Proton transfer to nitrogen has not occurred since the i.r. spectrum shows no $\nu(NH_2^+)$ band. Partial charge transfer has taken place which explains why the enol oxygen, rather than the carbonyl oxygen, acts as the acceptor for a second N–H hydrogen bond. The negative charge is localized on the enol oxygen, but in forming the second hydrogen bond there is a charge transfer along the NHO bond which results in the enol $R[C(1)–O(1)]$ being shorter than in other β-diketones where it is generally *ca.* 1.33 Å.[11]

Another 1:1 adduct of PD has been inferred for PD·H₂O in C₆H₆, and the PD is deduced to be in the enol tautomer.[17] In this instance proton transfer is unlikely but again this adduct may also have a bifurcated hydrogen bond.

The decomposition of PD·DEA produces the enaminone, 4-diethylaminopent-3-en-2-one.[3-5] Preliminary investigations into this reaction suggest that hydrogen bonding has an inhibiting effect on enaminone formation.

Experimental

Instruments.—I.r., Perkin Elmer 983G (KBr discs, Nujol and hexachlorobutadiene mulls); n.m.r., Bruker WM 250 (¹³C, 62.9 MHz; ¹H, 250 MHz); *X*-ray, Enraf-Nonius CAD-4 diffractometer.

Pentane-2,4-dione–Diethylamine 1:1 *Adduct.*—At, and above, 0.17 mol fraction of DEA in PD, crystals of the 1:1 adduct

PD·DEA separate from the mixture. The adduct is volatile and evaporates within minutes in the open. It can be stored in a sealed container at −10 °C without appreciable deterioration for several months. Attempts to mount crystals of PD·DEA for *X*-ray diffraction were hampered by their volatility.

The i.r. spectrum of PD·DEA is dominated by a very intense broad band centred at 3 430 cm⁻¹ which spans the range 3 600—2 600 cm⁻¹ and is typically a hydrogen-bonded absorption. Other bands in the spectrum are centred at 2 980s, 1 611s, (νC=O, νC=C) 1 500m, 1 451s, 1 405s, 1 358w, 1 140w, 1 007w, 910w, 760w, 620w, and 420w cm⁻¹. Partial decomposition of crystals of PD·DEA occurs on mulling or KBr disc preparation.

The ¹H n.m.r. spectrum of PD showed an upfield shift of the enol proton resonance from 15.40 in neat PD to 13.40 with 0.40 mol fraction of DEA present, beyond which concentration the signal was unobservable due to rapid proton transfer.

Crystal Data.—C₉H₁₉NO₂, MeCOCH₂COMe, (C₂H₅)₂NH, M = 173.25, monoclinic, a = 8.609(1), b = 7.376(1), c = 17.311(2) Å, β = 96.69(1)°, V = 1 091.714 Å³, $P2_1/c$, Z = 4, D_c = 1.05 g cm⁻³, $F(000)$ = 388, $\mu(Cu-K_\alpha)$ = 5.19 cm⁻¹, λ = 1.541 78 Å, T = 263 K. Of 2 063 unique intensity data measured, 986 were deemed observed [$I > 1.5\sigma(I)$].

Solution and Refinement of the Structure.—A crystal of suitable dimensions for *X*-ray work was cut from a larger block and rapidly sealed in a glass capillary as the complex was highly volatile. Intensity data were collected to a $\theta_{max.}$ of 70° on a Nonius CAD4 diffractometer using the $\omega - 2\theta$ scan mode.[19] Standard reflections monitored throughout data collection, at reduced temperature, indicated decay for which subsequent rescaling of the data was carried out followed by empirical absorption corrections.

The structure was solved using direct methods (SHELX84

Table 3. Hydrogen bonding distances (Å) for [PD·DEA]$_2$

N(1)···O(1)	2.755	N(1)···O(2)	2.797
H(1)···O(1)	1.514	H(1)···O(2)	2.165
H(11)···O(1)	2.781	H(11)···H(1)	1.738
O(1)···O(2)	2.920	N(1)···O(1a)	2.755
H(11)···O(1a)	1.774	H(11)···H(1a)	2.629

Key to symmetry operations relating designated atoms to reference atoms at (x, y, z); (a) $1.0 - x$, $-y$, $2.0 - z$

Table 4. Least squares planes

	Deviations from plane (Å) *	
	Plane 1	Plane 2
C(1)	0.0424	−0.1915
C(2)	0.0096 *	−0.1283
C(3)	−0.0107 *	−0.2150
C(4)	0.0062 *	−0.1282
C(5)	0.0125	−0.2235
O(1)	−0.0040 *	0.0 *
O(2)	−0.0012 *	0.0 *
N(1)	−0.2664	0.0 *
H(1)	−0.2167	−0.0928

* Atoms defining plane

program for crystal structure solution). Refinement by full-matrix least-squares[20] and difference Fourier maps revealed the remaining atoms. The final refinement cycle employed aniso-tropic thermal parameters for the non-hydrogen atoms, and isotropic thermal parameters for the hydrogens which were refined freely except that methyl hydrogens were given group thermal parameters. The secondary extinction coefficient was varied and coverged at 0.039. Final R values were $R = 0.0745$, $R_w = [\Sigma(w\Delta)^2/\Delta wF_o^2]^{\frac{1}{2}} = 0.0807$, where $w = 1/[\sigma^2(F_o) + 0.0014F_o^2]$.

Table 1 lists the atomic co-ordinates, Table 2 the bond lengths and angles, and Table 3 the hydrogen bonding dis-tances. Least-squares planes data are given in Table 4. Thermal parameters, full lists of hydrogen atom co-ordinates, hydrogen bond lengths and angles are available as a Supplementary Publication [Sup. No. 56468 (4 pp)].* Structure factor tables are available on request from the Editorial Office.

* For details of the Supplementary Publications Scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1986, Issue 1.

The structure is shown in Figure 1 and the hydrogen bonding shown diagramatically in Figure 2.

Acknowledgements

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