Acta Cryst. (1992). C**48**, 528–530

(*E*)-3-Dimethylamino-1,2-diphenyl-2-propen-1-one: Structure of an Enaminone

By M. I. Arriortua* and M. K. Urtiaga

Departamento de Mineralogía-Petrología, Universidad del País Vasco, Apartado 644, 48080 *Bilbao, Spain*

E. Domínguez,* A. Igartua and C. Iriondo

Departamento de Química Orgánica, Universidad del País Vasco, Apartado 644, 48080 *Bilbao, Spain*

and X. Solans

Departamento de Cristalografía, Mineralogía y Depósitos Minerales, Universidad de Barcelona,
Martí y Franqués s/n, 08028 *Barcelona, Spain*

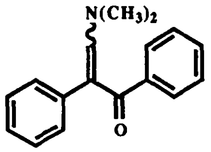
(*Received* 5 *February* 1991; *accepted* 12 *August* 1991)

Abstract. $C_{17}H_{17}NO$, $M_r = 251.33$, monoclinic, $P2_1/n$, $a = 11.596\,(2)$, $b = 14.757\,(3)$, $c = 8.126\,(1)$ Å, $\beta = 110.48\,(2)°$, $V = 1302.6\,(6)$ Å^3, $Z = 4$, $D_x = 1.281$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0.7107$ Å, $\mu(\mathrm{Mo}\ K\alpha) = 0.85$ cm^{-1}, $F(000) = 536$, $T = 298$ K, $R = 0.054$ for 1930 observed reflections. The crystal structure of the title compound shows it to be the *E,E* (*trans-s-trans*) isomer. The enaminone group is virtually planar, with the bonding delocalized, as the short N—C(3) [1.390 (3) Å] distance shows.

Introduction. Enaminones have already been established as synthetic intermediates, particularly in heterocyclic chemistry. For instance, they have been used for the preparation of pyrimidones, indoles and pyrrolopyridazines (Coppola, Hardtmann & Huegui, 1974), phenanthridine and acridine derivatives (Tilak, Berde, Gogte & Ravindranathan, 1970) and pyrazoles (Bailey & Powles, 1990), among others.

Taking into account that the enamino ketones possess five positions vulnerable to electrophilic attack and two to nucleophilic attack (Singer & Mass, 1987), it is easy to appreciate the interesting and sometimes rather complicated reactivity of the system under study (Greenhill, 1977).

In the course of our investigations directed towards the synthesis of nitrogen heterocycles with potential pharmacological activity, we have prepared 3-dimethylamino-1,2-diphenyl-2-propen-1-one (1) by direct reaction of benzyl phenyl ketone with *N,N*-dimethylformamide dimethyl acetal in benzene. The product had a sharp melting point and was homogeneous to thin-layer chromatography on silica gel in a variety of solvents. This behaviour together with the ^{1}H NMR spectral data indicated the product contained only one of the two possible stereoisomers (Igartua, 1991). In order to assign unambiguously the correct stereochemistry for the latter derivative, we have determined its X-ray crystal structure.



(1)

Experimental. Preliminary cell dimensions and space-group symmetry were obtained from Weissenberg and oscillation photographs. A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on an Enraf–Nonius CAD-4 diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections ($12 \leq \theta \leq 16°$) and refined by least squares. Intensities were collected with graphite-monochromatized Mo $K\alpha$ radiation, using ω–2θ scan technique. 2292 reflections were measured in the range $2 \leq \theta \leq 25°$ (h − 13→13, k 0→17, l 0→9). 1930 reflections were assumed as observed applying the condition $I \geq 2.5\sigma(I)$. R_{int} on $F = 0.014$. Three reflections were measured every 2 h as orientation and intensity control, significant intensity decay was not observed. Lorentz–polarization but no absorption corrections were made. Transformation (001, $0\bar{1}0$, 201) generates a pseudo-orthorhombic *C*-centred cell of dimensions $a = 8.126$, $b = 14.757$ and $c = 21.726$. However, the merging R for this cell is 0.31, clearly indicating that the Laue symmetry is not *mmm*.

The structure was solved by *MULTAN*11/84 (Main, Fiske, Hull, Lessinger, Germain, Declercq &

---

* Authors to whom correspondence should be addressed.

0108-2701/92/030528-03$03.00

Table 1. *Final fractional coordinates* ($\times 10^5$) *and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = (1/3)\Sigma_i \Sigma_j B_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	B_{eq}(Å^2)
N	13563 (16)	60243 (10)	24176 (21)	3.13 (7)
O	27076 (19)	35369 (10)	−4950 (22)	5.28 (8)
C(1)	4130 (27)	56388 (19)	31693 (42)	4.44 (12)
C(2)	14861 (26)	70023 (14)	25964 (34)	4.12 (10)
C(3)	19613 (17)	55746 (13)	14523 (23)	2.90 (8)
C(4)	20194 (17)	46615 (12)	11219 (23)	3.01 (7)
C(5)	25667 (19)	43471 (12)	−2374 (25)	3.41 (8)
C(6)	30075 (17)	50021 (13)	−14043 (24)	3.17 (7)
C(7)	23820 (20)	57499 (14)	−21183 (24)	3.73 (8)
C(8)	28409 (28)	63108 (17)	−32091 (30)	5.16 (11)
C(9)	39061 (34)	61317 (23)	−36118 (33)	6.26 (14)
C(10)	45389 (28)	53741 (26)	−29308 (35)	6.01 (15)
C(11)	40901 (21)	48140 (18)	−18464 (29)	4.51 (10)
C(12)	16126 (17)	39488 (12)	21994 (24)	2.99 (8)
C(13)	20919 (20)	38978 (14)	38913 (25)	3.51 (8)
C(14)	17324 (21)	32453 (15)	49094 (27)	3.95 (9)
C(15)	8698 (22)	26317 (15)	42512 (32)	4.22 (11)
C(16)	3841 (21)	26746 (15)	25745 (33)	4.37 (10)
C(17)	7575 (20)	33184 (13)	15529 (29)	3.76 (8)

Woolfson, 1984), and refined by the full-matrix least-squares method, with the *SHELX76* program (Sheldrick, 1976). The function minimized was $\Sigma w \| F_o | - | F_c \|^2$, where $w = [\sigma^2(F_o) + 0.00043(F_o)^2]^{-1}$, f, f' and f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Positions of 11 H atoms were located from a difference Fourier map and the remaining H atoms were calculated using a riding model. All H atoms were refined with an overall isotropic temperature factor. The final R factor was 0.054 ($wR = 0.059$) for all observed reflections. The number of refined parameters was 200. Maximum shift/e.s.d. = 0.06 for U_{33} of C(14). Maximum and minimum peaks in final difference synthesis were 0.2 and -0.2 e Å^{-3}, respectively.

The geometric calculations were performed with *XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) and *XANADU* (Roberts & Sheldrick, 1975), and molecular illustrations were drawn with *SCHAKAL88* (Keller, 1988).

Discussion. Final atomic coordinates for the non-H atoms are given in Table 1 and bond distances, angles and selected torsion angles in Table 2.* The above-mentioned investigations showed an *E*,*E* (*trans-s-trans*) conformation for the vinylogous amide under study (Fig. 1).

Table 2. *Bond distances* (Å), *angles* (°) *and selected torsion angles* (°) *characterizing the molecular conformation with e.s.d.'s in parentheses*

C(1)—N	1.536 (4)	C(2)—N	1.453 (2)
C(3)—N	1.390 (3)	C(5)—O	1.234 (2)
C(3)—C(4)	1.380 (3)	C(4)—C(5)	1.526 (3)
C(4)—C(12)	1.544 (3)	C(5)—C(6)	1.560 (3)
C(6)—C(7)	1.336 (3)	C(6)—C(11)	1.448 (4)
C(7)—C(8)	1.444 (4)	C(8)—C(9)	1.409 (5)
C(9)—C(10)	1.346 (5)	C(10)—C(11)	1.432 (4)
C(12)—C(13)	1.292 (3)	C(12)—C(17)	1.327 (3)
C(13)—C(14)	1.424 (3)	C(14)—C(15)	1.316 (3)
C(15)—C(16)	1.281 (3)	C(16)—C(17)	1.425 (4)
C(1)—N—C(2)	113.0 (2)	C(1)—N—C(3)	128.1 (2)
C(2)—N—C(3)	118.4 (2)	N—C(3)—C(4)	130.1 (2)
C(3)—C(4)—C(5)	119.9 (2)	C(3)—C(4)—C(12)	120.6 (2)
C(5)—C(4)—C(12)	119.4 (2)	O—C(5)—C(4)	122.0 (2)
O—C(5)—C(6)	114.0 (2)	C(4)—C(5)—C(6)	124.0 (2)
C(5)—C(6)—C(7)	122.1 (2)	C(5)—C(6)—C(11)	121.9 (2)
C(7)—C(6)—C(11)	115.9 (2)	C(6)—C(7)—C(8)	118.6 (2)
C(7)—C(8) C(9)	125.2 (2)	C(8)—C(9)—C(10)	117.2 (3)
C(9)—C(10)—C(11)	118.0 (3)	C(6)—C(11)—C(10)	125.1 (2)
C(4)—C(12)—C(13)	122.7 (2)	C(4)—C(12)—C(17)	126.0 (2)
C(13)—C(12)—C(17)	111.4 (2)	C(12)—C(13)—C(14)	123.6 (2)
C(13)—C(14)—C(15)	124.4 (2)	C(14)—C(15)—C(16)	112.8 (2)
C(15)—C(16)—C(17)	122.8 (2)	C(12)—C(17)—C(16)	125.0 (2)
O—C(5)—C(4)—C(12)	179.3 (2)	O—C(5)—C(6)—C(11)	143.1 (2)
O—C(5)—C(6)—C(7)	39.9 (2)	C(5)—C(4)—C(12)—C(17)	119.3 (2)
C(5)—C(4)—C(12)—C(13)	61.1 (2)	C(4)—C(3)—N—C(1)	169.8 (2)
C(4)—C(3)—N—C(2)	1.9 (2)	N—C(3)—C(4)—C(5)	10.4 (2)
N—C(3)—C(4)—C(12)	165.6 (2)	C(3)—C(4)—C(5)—C(6)	176.0 (2)
C(3)—C(4)—C(5)—O	4.6 (2)	C(4)—C(5)—C(6)—C(7)	139.6 (2)
C(4)—C(5)—C(6)—C(11)	37.5 (2)		

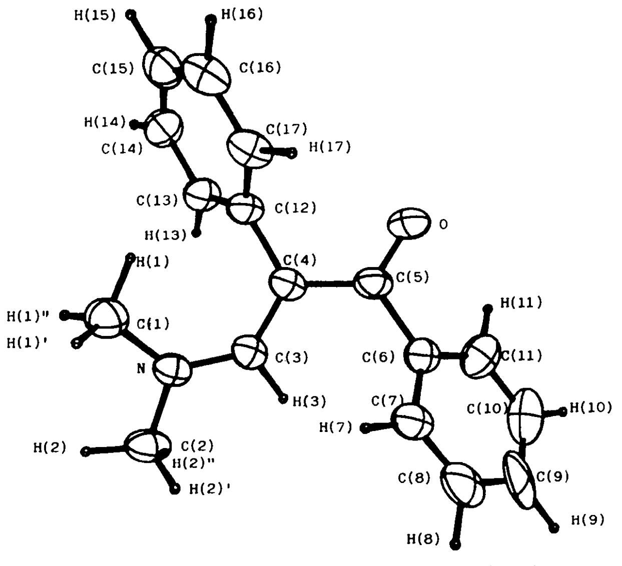


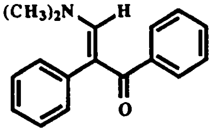
Fig. 1. Molecular structure of the compound showing the atom-numbering scheme.

Very few cases have been found in the literature of X-ray analyses of simple enaminones. In this context, the conformation in the solid phase of 4-*N*-pyrrolidyl-3-penten-2-one has been recently reported as *trans-s-cis*. (Emsley, Freeman, Parker, Kuroda &

---

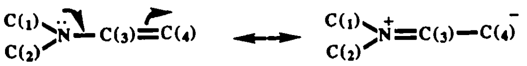
* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares-planes calculations and a view of the unit-cell packing have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54497 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Overill, 1987). The X-ray crystallographic study of (1) represents another example of this type of investigation.



(1)

As may be seen from Table 2, the shortening and lengthening of the N—C(3) [1.390 (3) Å] and C(3)—C(4) [1.380 (3) Å] bond lengths respectively, together with the observed enlargement of the C(4)—C(3)—N angle [130.1 (2)°], is likely to be related to the resonance between the double bond C(3)=C(4) and the electron pair at the N atom (Iida, Yuasa, Kibayashi & Iitaka, 1981). The enaminone system (N—C=C—C=O) is virtually planar. The largest deviations from the mean plane are C(5) 0.053 (2) and C(3) −0.068 (2) Å. Both benzene rings are planar within experimental error with a dihedral angle of 80.00 (7)° between the two benzene planes. Similar behaviour has been observed for other enaminones reported in the literature (Basato, Corain, Veronese, D'Angeli, Valle & Zanotti, 1984).



The conformation of this enaminone is described by the torsion angles given in Table 2.

We thank the Ministerio de Educación y Ciencia (Spain) for the grant of a fellowship to AI and the Dirección General de Investigación Científica y Técnica (DGICYT) (project No. PB87-0727).

References

Bailey, M. D. & Powles, G. R. (1990). US Patent No. 4,916,150, 10 April 1990.
Basato, M., Corain, B., Veronese, A. C., D'Angeli, F., Valle, G. & Zanotti, G. (1984). *J. Org. Chem.* **49**, 4696–4700.
Coppola, G. M., Hardtmann, E. & Huegui, B. S. (1974). *J. Heterocycl. Chem.* **11**, 51–56.
Emsley, J., Freeman, N. J., Parker, R. J., Kuroda, R. & Overill, R. E. (1987). *J. Mol. Struct.* **159**, 173–182.
Greenhill, J. V. (1977). *Chem. Soc. Rev.* pp. 277–294.
Igartua, A. (1991). Doctoral Thesis, Univ. del País Vasco, Bilbao, Spain.
Iida, H., Yuasa, Y., Kibayashi, C. & Iitaka, Y. (1981). *J. Chem. Soc. Dalton Trans.* pp. 2212–2216.
Keller, E. (1988). *SCHAKAL*88. A Fortran program for the graphic representation of molecular models. Univ. of Freiburg, Germany.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1984). *MULTAN*11/84. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
Roberts, P. & Sheldrick, G. M. (1975). *XANADU.* Program for crystallographic calculations. Univ. of Cambridge, England.
Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
Singer, B. & Mass, G. (1987). *Chem. Ber.* **120**, 1683–1690.
Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. W. & Hall, S. R. (1972). The *XRAY*72 system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
Tilak, B. D., Berde, H., Gogte, V. N. & Ravindranathan, T. (1970). *Indian J. Chem.* **8**, 1–4.

Acta Cryst. (1992). C**48**, 530–533

Structure of a Charge-Transfer Complex of 3,8-Diethyl-5,10-dimethyl-1,6-dioxapyrene (DEDMDOP) with 7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ)*

By Niels Thorup and Michael Hjorth

Structural Chemistry Group, Chemistry Department B, The Technical University of Denmark, DK-2800 Lyngby, Denmark

and Jørn B. Christensen and Klaus Bechgaard

Centre for Interdisciplinary Studies of Molecular Interactions, University of Copenhagen, Blegdamsvej 21, DK-2100 Copenhagen Ø, Denmark

(*Received* 8 *July* 1991; *accepted* 23 *August* 1991)

Abstract. $C_{20}H_{20}O_2.C_{12}H_4N_4$, $M_r = 496.57$, orthorhombic, $Pmnn$, $a = 6.749$ (1), $b = 9.699$ (2), $c = 19.204$ (1) Å, $V = 1257.1$ (3) Å^3, $Z = 2$, $D_x = 1.312$, $D_m = 1.291$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.781$ cm^{-1}, $F(000) = 520$, $T = 294$ K, $R = 0.062$ for 765 observed reflections. The structure is composed of stacks along the a axis of alternating DEDMDOP

---

* The IUPAC name for TCNQ is 2,2′-(2,5-cyclohexadiene-1,4-diylidene)bispropanedinitrile.

0108-2701/92/030530-04$03.00