The authors thank the Crystallographic Research Center, Institute for Protein Research, Osaka University, for the use of the facility.

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Acta Cryst. (1989). C**45**, 65–67

Structure of 4-[(2-Benzoyl-1-methyl)vinyleneimino]butyric Acid

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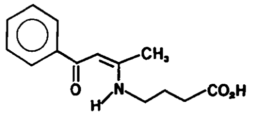
(*Received* 5 *May* 1988; *accepted* 25 *July* 1988)

Abstract. $C_{14}H_{17}NO_3$, $M_r = 247\cdot29$, monoclinic, $P2_1/n$, $a = 12\cdot109\,(5)$, $b = 10\cdot907\,(3)$, $c = 10\cdot846\,(3)$ Å, $\beta = 113\cdot06\,(2)°$, $V = 1318\cdot0\,(8)$ Å^3, $Z = 4$, $D_x = 1\cdot246$, $D_m = 1\cdot25$ g cm^{-3} (by flotation), $\lambda(\mathrm{Cu}\,K\alpha) = 1\cdot54178$ Å, $\mu = 6\cdot781$ cm^{-1}, $F(000) = 528$, $T = 298$ K, $R = 0\cdot0525$ for 1425 observed reflections. The enaminone system in the title compound is very nearly planar and has a *cis–s–cis* conformation. The resulting six-membered ring involves a hydrogen bond between the NH and the ketonic carbonyl. The conformation of the carboxypropyl fragment enables molecules related by a centre of symmetry to organize in dimeric structures characterized by hydrogen bonding between the two enaminone heteroatoms of one molecule and the carboxylic oxygens of the other.

Introduction. As part of a programme of synthesis of potential γ-aminobutyric acid (GABA) receptor agonists (Bartholini, 1985; Krogsgaard-Larsen, Falch & Hjeds, 1985) to be tested for central nervous system activity, we have prepared a series of imines of GABA with 1,3-dicarbonyl derivatives (Merlini & Arnoldi, 1988). The structure of the products, although supported by analytical and spectroscopic data, is open to the possibility of regioisomerism, geometrical isomerism and tautomerism.

Although examples of regioselective attack of amines onto aromatic 1,3-diones have been known for a long time (Beyer & Claisen, 1887), and tautomerism has been studied with the aid of NMR (Dudek & Holm, 1961, 1962) and UV spectroscopy (Ostercamp, 1970), the results are not completely unambiguous. Moreover, information about the conformation of the carboxypropylimino side chain would be useful for structure–activity studies.

Therefore we report here the crystal and molecular structure of the title compound (1), prepared from GABA and benzoylacetone. X-ray analysis of this kind of compound has been performed, to our knowledge, only on metal complexes (Iida, Yuasa, Kibayashi & Iitaka, 1981).



(1)

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Experimental. Colourless transparent single crystals of the title compound, prismatic in habit, were obtained by slow evaporation of a methanol solution.

A crystal of approximate dimensions 0·40 × 0·35 × 0·30 mm was mounted on a glass fibre in a general orientation and used for all analyses. Cell constants from counter data with least-squares fitting of 2θ values of 30 reflections with $2\theta \geq 25°$; Philips PW 1100 diffractometer (graphite-monochromated Cu $K\bar{\alpha}$ radiation), $8 \leq 2\theta \leq 110°$, $\omega/2\theta$ scans, scan speed $0{\cdot}025°\ \mathrm{s}^{-1}$, constant scan width 1·30°, two background counts at each side of the peak for half the peak measuring time and values averaged; 1659 independent reflections measured, 1425 of them considered observed by the criterion $I \geq 3\sigma(I)$ (based on counting statistics); *hkl* ranges $|h| \leq 12$, $k \leq 11$, $l \leq 11$, two standard reflections ($021, 02\bar{1}$) measured every 120 min to check crystal stability and experimental conditions, no significant variations detected; Lorentz and polarization but no absorption corrections.

Structure solved using *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). *E* map from highest figure of merit set revealed all but three non-hydrogen atoms; other atoms located by Fourier difference maps including all H atoms.

Blocked-matrix refinement with *SHELX*76 (Sheldrick, 1976), function minimized $\sum w(|F_o| - |F_c|)^2$, optimized weighting scheme $\{w = 1/[\sigma^2(F_o) + gF_o^2],\ g = 0{\cdot}009383\}$, thermal parameters anisotropic for non-hydrogen atoms, individual isotropic for hydrogens, reflections 020, 021, $\bar{2}11$, $\bar{3}11$, $\bar{3}12$ omitted from the refinement in the final cycles, final $R = 0{\cdot}0525$, $wR = 0{\cdot}0603$, $S = 0{\cdot}84$, $(\Delta/\sigma)_{\max} = 0{\cdot}4$, max. and min. heights in final Fourier map 0·25 and $-0{\cdot}24\ \mathrm{e\ \AA^{-3}}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974); geometrical calculations with *PARST* (Nardelli, 1983).*

Discussion. Final atomic coordinates are given in Table 1, while bond lengths and angles are reported in Table 2. In Fig. 1 a *PLUTO* (Motherwell & Clegg, 1978) view of the two centrosymmetrically related molecules shows both the conformational and the packing features of the title compound.

The phenyl group presents normal values for bond lengths and angles, corresponding to the substitution pattern (Domenicano, Murray-Rust & Vaciago, 1983). The dihedral angle between the phenyl and the *cis–s–cis* enaminone ring least-squares planes is 8·1 (1)° and the C9—C8 bond length of 1·491 (3) Å suggests limited

Table 1. *Final positional parameters* (× 10^4) *with e.s.d.'s on last significant figure in parentheses* [*equivalent isotropic temperature factors* B_{eq} (Å^2) (*Hamilton,* 1959)]

	x	y	z	B_{eq}
O1	4353 (2)	1174 (1)	−3491 (1)	6·0 (1)
O2	5149 (2)	223 (1)	−1539 (2)	6·4 (2)
C1	5051 (2)	1127 (2)	−2208 (2)	4·2 (2)
C2	5724 (2)	2288 (2)	−1686 (2)	4·6 (2)
C3	6381 (2)	2323 (2)	−182 (2)	4·7 (2)
C4	5545 (2)	2450 (2)	545 (2)	4·2 (2)
N1	6170 (1)	2330 (2)	1988 (2)	4·1 (1)
C5	6628 (2)	3222 (2)	2876 (2)	4·1 (2)
C6	6475 (3)	4516 (2)	2377 (2)	6·2 (2)
C7	7205 (2)	2994 (2)	4244 (2)	4·1 (2)
C8	7305 (2)	1835 (2)	4842 (2)	3·8 (2)
O3	6889 (1)	878 (1)	4150 (1)	5·1 (1)
C9	7898 (2)	1688 (2)	6326 (2)	3·8 (1)
C10	8516 (2)	2638 (2)	7179 (2)	4·2 (2)
C11	9050 (2)	2461 (2)	8554 (2)	5·0 (2)
C12	8993 (2)	1340 (2)	9093 (2)	5·5 (2)
C13	8399 (2)	386 (2)	8259 (2)	5·8 (2)
C14	7857 (2)	562 (2)	6899 (2)	4·9 (2)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C1—O1	1·316 (2)	C9—C8	1·491 (3)
C1—O2	1·202 (3)	C10—C9	1·396 (3)
C2—C1	1·491 (3)	C14—C9	1·387 (3)
C3—C2	1·509 (3)	C11—C10	1·387 (3)
C4—C3	1·514 (4)	C12—C11	1·369 (4)
N1—C4	1·454 (2)	C13—C12	1·381 (3)
C5—N1	1·328 (2)	C14—C13	1·373 (3)
C6—C5	1·497 (3)	HO1—O1	0·89 (2)
C7—C5	1·393 (3)	HN—N1	0·85 (2)
C8—C7	1·405 (3)	⟨C—H⟩	0·97 (7)*
O3—C8	1·269 (2)		

O2—C1—O1	122·7 (2)	C9—C8—O3	117·5 (2)
C2—C1—O1	113·4 (2)	C10—C9—C8	122·8 (2)
C2—C1—O2	123·8 (2)	C14—C9—C8	119·5 (2)
C3—C2—C1	114·2 (2)	C14—C9—C10	117·7 (2)
C4—C3—C2	112·9 (2)	C11—C10—C9	120·8 (2)
N1—C4—C3	112·4 (2)	C12—C11—C10	120·2 (2)
C5—N1—C4	127·5 (2)	C13—C12—C11	119·6 (2)
C6—C5—N1	118·1 (2)	C14—C13—C12	120·4 (2)
C7—C5—N1	122·3 (2)	C13—C14—C9	121·3 (2)
C7—C5—C6	119·6 (2)	HO1—O1—C1	110 (2)
C8—C7—C5	124·7 (2)	HN—N1—C4	119 (1)
O3—C8—C7	121·6 (2)	HN—N1—C5	112 (1)
C9—C8—C7	120·8 (2)		

* Standard deviation from the mean according to the expression $\sigma(\bar{x}) = [\sum(x_i - \bar{X})^2/(n-1)]^{1/2}$.

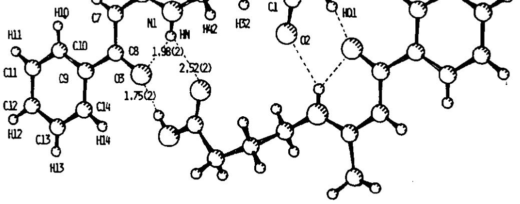

Fig. 1. View of the title compound with details of the hydrogen bond responsible for dimerization.

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* Hydrogen-atom positional parameters, anisotropic thermal parameters, a list of observed and calculated structure factors, torsion angles and least-squares-planes calculation details have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51279 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

interactions between the π orbitals of the two groups. Similarly to other systems with polarized double bonds (Ganazzoli, Meille & Gronchi, 1986), the enaminone ring shows extensive π delocalization involving both the carbonyl and the aminic N which displays the features of sp^2 hybridization. The N1—C5—C7—C8 torsion angle is −4·0 (4)°, while C5—C7—C8—C9 and C4—N1—C5—C7 measure −177·5 (2) and 179·6 (2)° respectively. As a consequence the deviations of atoms C9, C8, O3, C7, C5, N1, C4 from the least-squares planes they define are within 0·19 (3) Å, while HN and C6 are at distances of 0·08 (2) and 0·138 (4) Å respectively from the same plane. It is noteworthy that the bond lengths and angles of the enaminone ring in the title compound are insignificantly different from the corresponding values found in *cis–s–cis* enaminones coordinated to Pd (Iida, Yuasa, Kibayashi & Iitaka, 1981) possibly also because of the large standard deviations involved in that structural analysis.

The carboxypropyl chain bond lengths and angles are also in the expected ranges but its conformation is of interest. The C3—C4—N1—C5, the C2—C3—C4—N1 and the O1—C1—C2—C3 torsion angles are 93·1 (3), 172·8 (2) and 171·2 (2)° respectively while C1—C2—C3—C4 is −71·8 (3)°. This arrangement brings O1, O2 and HO1 close to the enaminone plane and is probably due to the formation of dimeric structures (Fig. 1) in which the enaminone heteroatoms of one molecule are hydrogen bonded to the carboxyl O atoms of the molecule related by the $(-x+1, -y, -z)$ symmetry operator to the original one. The shorter hydrogen bonds involve both intra- and intermolecularly the ketone rather than the carboxyl carbonyl oxygen as acceptor. Since ketonic carbonyls are known (Taylor & Kennard, 1984) to be better acceptors than un-ionized carboxyls, this feature may account for the formation of the peculiar dimers found in the crystal structure of the title compound.

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Acta Cryst. (1989). C**45**, 67–71

Anti-Cancer Compounds. Structures of the Dimethyl[2-(1,8-naphthalenedicarboxido)ethyl]ammonium Cation with Cl^-, $PtCl_4^{2-}$, $PtCl_6^{2-}$ and $PtCl_3[HN(CH_3)_2]^-$ Anions

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(*Received* 18 *April* 1988; *accepted* 1 *August* 1988)

Abstract. (1): Dimethyl[2-(1,8-naphthalenedicarboximido)ethyl]ammonium chloride, $C_{16}H_{17}N_2O_2^+.Cl^-$, $M_r = 304·6$, monoclinic, $P2_1/c$, $a = 13·261$ (1), $b = 12·099$ (1), $c = 10·693$ (2) Å, $\beta = 118·02$ (1)°, $V = 1514·4$ (3) Å^3, $Z = 4$, $D_m = 1·34$, $D_x = 1·336$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1·5418$ Å, $\mu = 2·63$ cm^{-1}, $F(000) = 640$, $T = 293$ K, $R = 0·040$ for 2531 reflections. (2): Dimethyl[2-(1,8-naphthalenedicarboximido)ethyl]ammonium tetrachloroplatinate(II), $(C_{16}H_{17}N_2O_2^+)_2.[PtCl_4]^{2-}$, $M_r = 875·5$, monoclinic, $P2_1/c$, $a = 12·548$ (1), $b = 8·957$ (1), $c = 14·829$ (1) Å, $\beta = 105·95$ (1)°, $V = 1602·6$ (2) Å^3, $Z = 2$, $D_m = 1·82$,

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