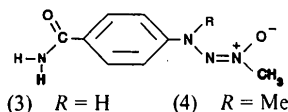


Vaughan, 1992). The presence of the O(1)—H(N1) hydrogen bond manifests itself by giving (2) considerably more planar character compared to (1). For example, the six atoms O(1)—C(7)—C(2)—C(1)—N(1)—H(N1) are close to lying in a plane ( $\chi^2 = 12.3$ , maximum deviation = 0.03 Å), as are the *N*-oxide group ( $\chi^2 = 2.84$ , maximum deviation = 0.005 Å) and the ester moiety ( $\chi^2 = 1.5$ , maximum deviation = 0.005 Å). The dihedral angles between planes are much smaller in compound (2) than in compound (1): between the *N*-oxide group and the phenyl ring the dihedral angle is 0.71°, and between the phenyl ring and the ester group the dihedral angle is 3.57°. There are no short intermolecular contacts or unusual features in the cell packing (Fig. 4).



In conclusion, it is of interest to compare the bond-length data for (1) and (2) with the analogous data previously reported for the amides (3) and (4), tabulated in Table 4, and there is a considerable measure of agreement. In all cases, N(2)—N(3) is shorter than N(1)—N(2), consistent with the molecules adopting the *N*-oxide tautomeric form.

The authors are grateful to the following agencies for financial support: Natural Sciences and

Engineering Council of Canada, Saint Mary's University (Senate Research and purchase of the X-ray diffractometer).

#### References

- CAMERON, L. M., HOOPER, D. L. & VAUGHAN, K. (1992). *Can. J. Chem.* In the press.
- GABE, E. J., LE PAGE, Y., CHARLAND, J.-P., LEE, F. L. & WHITE, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- GIUMANINI, A. G., LASSIANI, L., NISI, C., PETRIC, A. & STANOVNIK, B. (1983). *Bull. Chem. Soc. Jpn*, **56**, 1887–1888.
- HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*. New York: Benjamin.
- HOOPER, D. L. & VAUGHAN, K. (1981). *J. Chem. Soc. Perkin Trans. 2*, pp. 1161–1165.
- JOESTEN, M. D. & SCHAAD, L. J. (1974). *Hydrogen Bonding*. New York: Marcel Dekker.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- KURODA, R. & WILMAN, D. E. V. (1985). *Acta Cryst.* **C41**, 1543–1545.
- MIESEL, J. L. (1976). US Patent No. 3962434.
- MITSUHASHI, T., OSAMURA, Y. & SHIMAMURA, O. (1965). *Tetrahedron Lett.* **30**, 2593–2596.
- NEIDLE, S., WEBSTER, G. D., KURODA, R. & WILMAN, D. E. V. (1987). *Acta Cryst.* **C43**, 674–676.
- SAMANTA, C., DE, P. K., SARKAR, S. B., SAHA, S. C. & TALAPATRA, S. K. (1985). *Acta Cryst.* **C41**, 142–144.
- VAUGHAN, K. (1977). *J. Chem. Soc. Perkin Trans. 2*, pp. 17–20.
- VAUGHAN, K. & WILMAN, D. E. V. (1991). *J. Chem. Res.* pp. 294–295.
- WILMAN, D. E. V. (1985). *Triazene N-Oxides*. In *Proceedings of the 3rd International Symposium on the Biological Oxidation of Nitrogen in Organic Molecules*, edited by J. W. GORROD & L. A. DAMANI, pp. 297–302. Chichester: Ellis Horwood.

*Acta Cryst.* (1992). **C48**, 1988–1991

## Intramolecular Interactions in 3,3'-Dinitro-2,2'-bipyridine

BY C. R. RICE AND J. D. WALLIS\*

*The Chemical Laboratory, University of Kent, Canterbury CT2 7NH, England*

AND D. C. POVEY

*Department of Chemistry, University of Surrey, Guildford, Surrey GU2 5XH, England*

(Received 31 December 1991; accepted 17 March 1992)

**Abstract.**  $C_{10}H_6N_4O_4$ ,  $M_r = 246.2$ , monoclinic,  $P2_1/c$ ,  $a = 8.259$  (7),  $b = 13.111$  (4),  $c = 9.978$  (4) Å,  $\beta = 104.90$  (5)°,  $V = 1044.1$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.57$  g cm<sup>-3</sup>, Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu = 1.2$  cm<sup>-1</sup>,  $F(000) = 504$ ,  $T = 293$  K,  $R = 0.035$ , for 1612 reflections. In the solid-state structure of the title compound, attractive intramolecular interactions in-

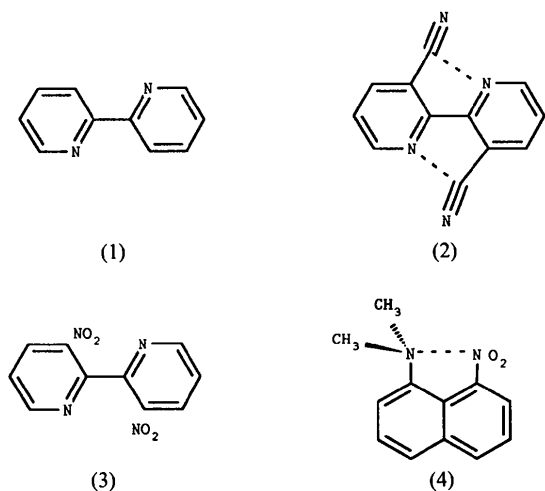
volving donation of electron density from nitro O atoms to the C(2) atoms of the opposite rings are more significant than those involving donation of lone-pair electron density to the nitro N atoms from ring N atoms.

**Introduction.** 2,2'-Bipyridine adopts an *anti* coplanar conformation (1) in the solid and gas phases (Chisholm, Huffman, Rothwell, Bradley, Kress &

\* To whom correspondence should be addressed.

Woodruff, 1981; Almenningen, Bastiansen, Gundersen & Samdal, 1989). Substituents in the 3 and 3' positions will cause the pyridine rings to rotate well away from coplanarity to minimize steric interactions. However, if the substituent can accept electron density 'through space' from the lone pair of the N atom belonging to the other ring, this effect may be considerably reduced. Recently we reported the structure of the 3,3'-dinitrile (2) (Baxter, Connor, Povey & Wallis, 1991) in which there are indeed short attractive intramolecular interactions between each ring N atom and the nitrile C atom attached to the opposite ring [ $C\cdots N$  2.695 (2) and 2.740 (2) Å]. The angle between the best planes of the aromatic rings is only 23.6 (1)°. These interactions may be interpreted as incipient chemical reactions between nucleophilic N atoms and electrophilic triple bonds: the  $C-C\equiv N$  groups are bent by *ca* 9° from linearity and the molecule has distorted to maximize the  $N\cdots C\equiv N$  angles (*ca* 108°).

To investigate whether such effects still pertain when the acceptor is an  $sp^2$  atom rather than an  $sp$  one, we have determined the structure of the 3,3'-dinitro derivative (3). Access to an  $sp^2$  atom is more restricted since such a substituent has a plane of symmetry rather than a  $C_\infty$  axis. Furthermore, the group must sacrifice some conjugation with the aromatic ring if it is to be suitably oriented to receive electron density from the pyridine N atom. Attractive interactions between amino N atoms and nitro N atoms have been observed in the *peri*-naphthalene (4) (Egli, Wallis & Dunitz, 1986).



**Experimental.** Large pale yellow crystals of (3), prepared by coupling of 2-chloro-3-nitropyridine (Kanoktanaporn & MacBride, 1978), were grown from hot 1,4-dioxan; m.p. 484–485 K. A crystal of dimensions 0.40 × 0.25 × 0.20 mm was used for data collection on an Enraf-Nonius CAD-4 diffractom-

eter with Mo  $K\alpha$  radiation, graphite monochromator and  $\omega$ - $2\theta$  scans. Unit-cell dimensions were determined by least-squares fit to setting angles of 25 automatically centred reflections with  $11 < \theta < 14^\circ$ . Measurements were performed at room temperature. No absorption correction was applied. Maximum ( $\sin\theta/\lambda$ ) in intensity measurements was  $0.62 \text{ \AA}^{-1}$ . One standard reflection was monitored and showed maximum variation of 2%. 2286 reflections were measured, of which 2036 were unique ( $R_{\text{int}} = 0.026$ ) and 1612 were counted as observed [ $I > 3\sigma(I)$ ]. Index range was  $h$  0/11,  $k$  0/17,  $l$  -12/12.  $0k0$  reflections were absent for  $k = \text{odd}$ ,  $h0l$  were absent for  $l = \text{odd}$ . The structure was solved in  $P2_1/c$  (SHELXS86; Sheldrick, 1986) and refined on  $F$  by full-matrix least-squares analyses including anisotropic displacement parameters for non-H atoms (SHELXL76; Sheldrick, 1976). H-atom positions were located in a difference Fourier map and refined with isotropic displacement parameters. With a weighting scheme  $w = [\sigma^2(F) + 0.0003F^2]^{-1}$ , the model converged to  $R = 0.035$ ,  $wR = 0.038$ . Maximum  $\Delta/\sigma$  in the final cycle for non-H atoms: positional parameters 0.006; displacement parameters 0.011; for H atoms 0.029 and 0.012, respectively. 187 parameters were refined. Maximum and minimum residual electron densities in the final difference Fourier synthesis were 0.14 and  $-0.21 \text{ e \AA}^{-3}$ . Computer programs: solution and refinement by SHELXS86 (Sheldrick, 1986) and SHELXL76 (Sheldrick, 1976); molecular illustrations with PLATON91 and PLUTON91 (Spek, 1991); and geometry calculations with PARST91 (Nardelli, 1991). Atomic scattering factors for O, N and C atoms were taken from Cromer & Mann (1968), for H atoms from Stewart, Davidson & Simpson (1965).

**Discussion.** The structure of (3) is illustrated in Figs. 1 and 2; fractional atomic coordinates and equivalent isotropic displacement parameters for non-H atoms are given in Table 1 and bond lengths and angles in Table 2.\* The pyridine rings, *A* and *B*, have a dihedral angle of  $42.9 (1)^\circ$  between them, such that each ring N atom lies adjacent to the nitro N atom attached to the opposite ring. The intramolecular  $N\cdots N$  distances [ $N(1A)\cdots N(7B)$  2.860 (2) and  $N(1B)\cdots N(7A)$  2.913 (2) Å] are just within the sum of the van der Waals radii for two N atoms (3.0 Å). However, the nitro-group planes are at  $42.8 (1) (A)$  and  $52.0 (1) (B)$  to their respective aromatic rings so that each O(8) atom approaches the C(2) atom of the

\* Lists of structure factors, anisotropic displacement parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55299 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0537]

other ring [O(8A)⋯C(2B) 2.916 (2) and O(8B)⋯C(2A) 2.980 (3) Å]. Of these two sets of two similar (but non-equivalent) interactions the O⋯C interactions appear to have the greater significance. Each C(2) atom is displaced from the plane of its three bonded neighbours towards the incipient O(8) atom [by 0.047 (2) and 0.048 (2) Å]. The O(8)⋯C(2) vectors make angles of 125.4 (1) and 124.5 (1)° with the corresponding C(2)—C(3) bonds and the N(7)—O(8)⋯C(2)—C(3) torsion angles are 159.1 (2) and 165.1 (2)°; not too different from the ideal geometry for an incipient Michael reaction (angle *ca* 110° and torsion *ca* 180°). Interactions of nitro O atoms with electron-deficient atoms (nitro and diazonium N atoms, and a nitrile C atom) have been observed before (Ciechandrowicz-Rutkowska, 1977; Wallis & Dunitz, 1984; Procter, Britton & Dunitz, 1981).

In contrast, the nitro groups are only pyramidalized slightly towards the adjacent pyridine N atoms [nitro N atoms lie 0.011 (2) and 0.012 (2) Å out of the planes defined by their bonded neighbours], although the N(1)⋯N(7) distances are within

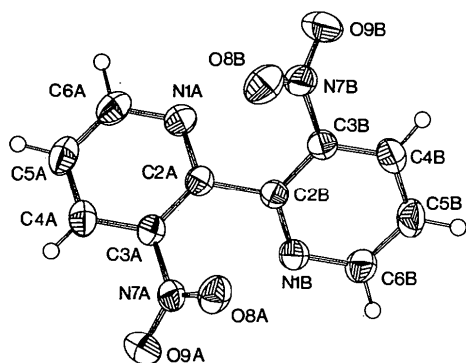


Fig. 1. View of (3) with atom labels and anisotropic displacement parameters drawn at the 50% level.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for (3)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	<i>U</i> <sub>eq</sub>
O(8A)	0.2680 (2)	0.6521 (1)	0.1270 (1)	0.0495 (6)
O(9A)	0.4949 (2)	0.6955 (1)	0.2762 (1)	0.0669 (8)
N(1A)	0.1975 (2)	0.4323 (1)	0.4055 (1)	0.0420 (7)
N(7A)	0.3642 (2)	0.6476 (1)	0.2416 (1)	0.0388 (7)
C(2A)	0.2496 (2)	0.4873 (1)	0.3119 (2)	0.0330 (7)
C(3A)	0.3191 (2)	0.5832 (1)	0.3461 (1)	0.0334 (7)
C(4A)	0.3429 (2)	0.6218 (1)	0.4777 (2)	0.0418 (8)
C(5A)	0.2892 (2)	0.5643 (2)	0.5731 (2)	0.0481 (9)
C(6A)	0.2151 (2)	0.4718 (1)	0.5316 (2)	0.0478 (9)
O(8B)	-0.1088 (2)	0.4492 (1)	0.1686 (1)	0.0594 (8)
O(9B)	-0.0938 (2)	0.2845 (1)	0.1787 (1)	0.0691 (9)
N(1B)	0.3817 (2)	0.4426 (1)	0.1335 (1)	0.0394 (7)
N(7B)	-0.0409 (2)	0.3683 (1)	0.1580 (1)	0.0448 (7)
C(2B)	0.2448 (2)	0.4345 (1)	0.1791 (1)	0.0325 (7)
C(3B)	0.1142 (2)	0.3712 (1)	0.1130 (2)	0.0349 (7)
C(4B)	0.1249 (2)	0.3125 (1)	0.0013 (2)	0.0425 (8)
C(5B)	0.2661 (2)	0.3221 (1)	-0.0453 (2)	0.0458 (9)
C(6B)	0.3890 (2)	0.3883 (1)	0.0217 (2)	0.0452 (8)

Table 2. Bond lengths (Å) and angles (°) for (3)

O(8A)—N(7A)	1.215 (2)	O(8B)—N(7B)	1.217 (2)
O(9A)—N(7A)	1.218 (2)	O(9B)—N(7B)	1.219 (2)
N(1A)—C(2A)	1.336 (2)	N(1B)—C(2B)	1.327 (2)
N(1A)—C(6A)	1.333 (2)	N(1B)—C(6B)	1.337 (2)
N(7A)—C(3A)	1.463 (2)	N(7B)—C(3B)	1.462 (2)
C(2A)—C(3A)	1.388 (2)	C(2B)—C(3B)	1.386 (2)
C(2A)—C(2B)	1.486 (2)	C(3B)—C(4B)	1.376 (2)
C(3A)—C(4A)	1.374 (2)	C(4B)—C(5B)	1.367 (3)
C(4A)—C(5A)	1.374 (2)	C(5B)—C(6B)	1.372 (3)
C(5A)—C(6A)	1.374 (3)		
C(2A)—N(1A)—C(6A)	118.3 (1)	C(2B)—N(1B)—C(6B)	117.9 (1)
O(8A)—N(7A)—O(9A)	124.0 (1)	O(8B)—N(7B)—O(9B)	125.3 (2)
O(8A)—N(7A)—C(3A)	118.3 (1)	O(8B)—N(7B)—C(3B)	117.6 (1)
O(9A)—N(7A)—C(3A)	117.7 (1)	O(9B)—N(7B)—C(3B)	117.1 (2)
N(1A)—C(2A)—C(3A)	120.3 (1)	N(1B)—C(2B)—C(2A)	116.0 (1)
N(1A)—C(2A)—C(2B)	115.6 (1)	N(1B)—C(2B)—C(3B)	120.8 (1)
C(3A)—C(2A)—C(2B)	123.8 (1)	C(2A)—C(2B)—C(3B)	122.8 (1)
N(7A)—C(3A)—C(2A)	120.9 (1)	N(7B)—C(3B)—C(2B)	120.4 (1)
N(7A)—C(3A)—C(4A)	117.9 (1)	N(7B)—C(3B)—C(4B)	118.5 (1)
C(2A)—C(3A)—C(4A)	121.2 (1)	C(2B)—C(3B)—C(4B)	121.0 (1)
C(3A)—C(4A)—C(5A)	117.9 (2)	C(3B)—C(4B)—C(5B)	117.5 (2)
C(4A)—C(5A)—C(6A)	118.3 (2)	C(4B)—C(5B)—C(6B)	118.8 (2)
N(1A)—C(6A)—C(5A)	124.0 (2)	N(1B)—C(6B)—C(5B)	123.8 (2)

Table 3. Deviations (Å × 10<sup>3</sup>) from best planes through the six ring atoms of each pyridine ring

	Ring A	Ring B
N(1)	-7 (2)	-10 (2)
C(2)	-11 (2)	-6 (2)
C(3)	18 (2)	16 (2)
C(4)	-9 (2)	-10 (2)
C(5)	-9 (2)	-5 (2)
C(6)	17 (2)	15 (2)
N(7)	124 (2)	116 (2)
C(2)*	-197 (2)	-181 (2)

\* Refers to the C(2) atom *not* belonging to the defined plane.

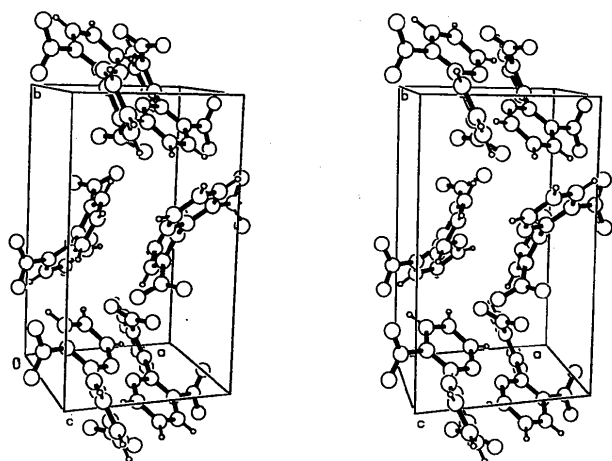


Fig. 2. Stereoview of the crystal packing of (3) viewed along the *c* axis.

van der Waals contact. Furthermore, the axis of each pyridine N lone pair makes an angle of 51.4 (2)° [for N(1A)] or 51.9 (2)° [for N(1B)] with the corresponding N(1)⋯N(7) vector, much larger than is observed in the seven structures of (4) (15–27°). Indeed, the N⋯N distances in (4) are considerably shorter [2.64 (1)–2.72 (1) Å] and the nitro groups more pyramidal. In (4), such interactions were probably the least-unfavourable orientations between these congested groups. In (3), both pyridine rings are

distorted into slight 'boat' conformations (Table 3) with the C(3) and C(6) atoms at the apices, distortions which act to move each nitro group away from the incipient lone pair. There are no especially short intermolecular interactions (Fig. 2).

We thank the University of Kent for a studentship to CRR.

#### References

- ALMENNINGEN, A., BASTIANSEN, O., GUNDERSEN, S. & SAMDAL, S. (1989). *Acta Chem. Scand.* **43**, 932–937.  
 BAXTER, P. N. W., CONNOR, J. A., POVEY, D. C. & WALLIS, J. D. (1991). *J. Chem. Soc. Chem. Commun.* pp. 1135–1137.  
 CHISHOLM, M. H., HUFFMAN, J. C., ROTHWELL, I. P., BRADLEY, P. G., KRESS, N. & WOODRUFF, W. H. (1981). *J. Am. Chem. Soc.* **103**, 4945–4947.  
 CIECHANDROWICZ-RUTKOWSKA, M. (1977). *J. Solid State Chem.* **22**, 185–192.  
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.  
 EGLI, M., WALLIS, J. D. & DUNITZ, J. D. (1986). *Helv. Chim. Acta*, **69**, 255–266.  
 KANOKTANAPORN, S. & MACBRIDE, J. A. H. (1978). *J. Chem. Soc. Perkin Trans. 1*, pp. 1126–1131.  
 NARDELLI, M. (1991). *PARST91*. Program for molecular geometry calculation. Univ. of Parma, Italy.  
 PROCTER, G., BRITTON, D. & DUNITZ, J. D. (1981). *Helv. Chim. Acta*, **64**, 471–477.  
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 SHELDRIK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.  
 SPEK, A. L. (1991). *PLUTON91*; *PLATON91*. Programs for molecular illustrations. Univ. of Utrecht, The Netherlands.  
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.  
 WALLIS, J. D. & DUNITZ, J. D. (1984). *Acta Cryst.* **A40**, C-106.

*Acta Cryst.* (1992). **C48**, 1991–1994

## Structure and Conformation of *N*-(4-Methyl-2-pyridyl)-*p*-chlorophenylsuccinimide

BY J. KAROLAK-WOJCIECHOWSKA AND W. KWIATKOWSKI

*Institute of General Chemistry, Technical University, 90-924 Łódź, Poland*

Z. KARCZMARZYK

*Department of Chemistry, Agriculture and Teachers University, 08-110 Siedlce, Poland*

AND A. ZEJC AND J. OBNISKA

*Department of Pharmaceutical Chemistry, Medicinal Academy, Kraków, Poland*

(Received 3 June 1991; accepted 4 March 1992)

**Abstract.** 3-(3-Chlorophenyl)-1-(4-methyl-2-pyridyl)-2,5-pyrrolidinedione,  $C_{16}H_{13}ClN_2O_2$ ,  $M_r = 300.74$ , triclinic,  $P\bar{1}$ ,  $a = 10.330$  (2),  $b = 10.958$  (2),  $c = 13.251$  (3) Å,  $\alpha = 78.48$  (2),  $\beta = 80.86$  (2),  $\gamma = 87.04$  (3)°,  $V = 1450.8$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.377$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $\mu = 2.4$  mm<sup>-1</sup>,  $F(000) = 624$ ,  $T = 293$  K, final  $R = 0.065$  for 3257 reflections selected from 4928 unique data according to the criterion  $I > 4\sigma(I)$ . Two molecules in the independent part of the unit cell are indicated as conformational isomers resulting from phenyl- and pyridyl-ring rotations. Both forms are not too far from the energetically equivalent minima on the conformation map (molecular-mechanics calculation).

**Introduction.** The present work refers to comprehensive studies on the structure–activity relationship in phenylsuccinimide anticonvulsants (Łucka-Sobstał, Zejc & Obniska, 1977; Lange, Rump, Ilczuk,

Łapszewicz, Rabsztyn & Walczyna, 1977; Lange, Rump, Gałęcka, Ilczuk, Lechowska-Postek, Rabsztyn, Szymańska & Walczyna, 1977; Łapszewicz, Lange, Rump & Walczyna, 1978; Chmielewska, 1983, 1984; Zejc & Obniska, 1984; Zejc, Obniska, Chojnacka-Wójcik, Tatarczyńska & Wiczyńska, 1987). All derivatives from this class of compound subjected to our earlier X-ray structure investigations (Kwiatkowski, Karolak-Wojciechowska, Obniska & Zejc, 1990; Kwiatkowski & Karolak-Wojciechowska, 1990, 1991, 1992a) reveal pharmacological activity, while the title compound is inactive. It was, therefore, of interest to solve the structure of the inactive derivative and thus gain the three-dimensional data required for comparison with the active succinimides (Kwiatkowski & Karolak-Wojciechowska, 1992b).

**Experimental.** The title compound recrystallized from ethanol to give colourless crystals. Unit-cell