equipment. BAH wishes to acknowledge the National Science Foundation for receipt of a CAREER award.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1246). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Abboud, K. A., Toporek, S. S. & Horenstein, B. A. (1996). *Acta Cryst.* C**53**, 118–120.

Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., Macrae, C. F., Mitchell, E. M., Mitchell, G. F., Smith, J. M. & Watson, D. G. (1991). *J. Chem. Inf. Comput. Sci.* **31**, 187–204.

Bucourt, R. (1974). In *Topics in Stereochemistry*, Vol. 8, edited by E. L. Eliel & N. L. Allinger. New York: Wiley Intersience.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Grundler, G. & Schmidt, R. R. (1985). *Carbohydr. Res.* **43**, 203–218.

Jones, P. G., Sheldrick, G. M., Kirby, A. J. & Glenn, R. (1982). *Z. Kristallogr.* **161**, 237–243.

Sheldrick, G. M. (1995). *SHELXTL*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1995). *SMART* and *SAINT. Data Collection and Processing Software for the SMART System.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1997). C**53**, 744–746

N,*N*-Diacetyl-2,5-dimethyl-6-nitroaniline†

Alan R. Kennedy and Abedawn I. Khalaf

Department of Pure & Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, Scotland. E-mail: a.r.kennedy@ccsun.strath.ac.uk

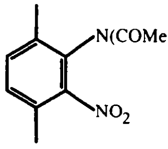
(*Received 1 October 1996; accepted 10 February 1997*)

Abstract

The diacetylamino moiety of the title compound, $C_{12}H_{14}N_2O_4$, is shown to adopt a *syn–anti* conformation and is twisted away from the perpendicular to the aryl ring.

Comment

During ongoing research on heterocyclic compounds with medicinal activity, the synthesis of *N*-acetyl-2,5-dimethyl-6-nitroanilide was sought (Suzuki, Ishibashi, Murashima & Tsukamoto, 1991; Sotomatsu, Shigemura, Murata & Fujita, 1993). No reaction took place between 2,5-dimethyl-6-nitroaniline and acetic anhydride at room temperature, but on heating overnight *N*,*N*-diacetyl-2,5-dimethyl-6-nitroaniline, (I), was produced, with no traces of the monoacetylated product. The crystal structure determination was undertaken in order to gain information on the conformation of the diacetylaniline fragment.



(I)

The crystal structure of (I) was found to consist of discrete molecules, with no intermolecular contacts significantly less than the sum of van der Waals radii. The internal angles of the highly substituted benzene ring display wide variations from trigonal geometry. The range is 115.6 (3)–123.3 (3)° (Table 1) which can be explained by the inductive effects of the substituents (Domenicano, 1992). Similarly the aryl ring bond distances span the range 1.364 (6)–1.392 (4) Å. The widening of the C(2)—C(1)—C(6) angle observed in *p*-bis(diacetylamino)benzene (Beagley, Flowers, Hafees & Pritchard, 1987) is cancelled in (I) by the large inductive effect of the *ortho*-NO_2 group.

As may be expected, atoms C(10), O(1), C(9), N(1) and C(11) in compound (I) are coplanar, while a twist about the N(1)—C(11) bond displaces the O(2) and C(12) atoms from this plane (Table 1. The diacetylamino (DAA) group adopts a *syn–anti* conformation with respect to the aryl ring and is shifted away from the perpendicular to the ring plane [C(2)—C(1)—N(1)—C(9) −104.0 (4) and C(2)—C(1)—N(1)—C(11) 77.9 (4)°]. A search of the Cambridge Structural Database (Allen & Kennard, 1993) found further structures (Irving & Irving, 1989; Reboul, Pepe, Siri, Odden, Rahal, Soyfer & Barbe, 1992; Reboul, Rahal, Pepe, Odden, Siri, Astier, Soyfer & Barbe, 1992; Wieckowski & Kry-

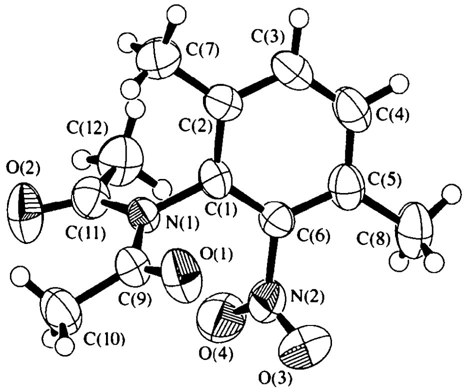


Fig. 1. The molecular structure of compound (I) with the atomic numbering. Non-H atoms are shown as 50% probability ellipsoids and H atoms as small spheres of arbitrary size.

---

† Alternative name: 3,6-dimethyl-2-nitrophenyldiacetamide.

gowski, 1981) to give a total of nine DAA fragments bonded to aryl rings. All fragments have the same *syn–anti* conformation as compound (I) and the following points are noted: the angle about the N(1) atom subtended by the aryl ring and the *syn*-carbonyl group is always small [range 114.4 (4)–116.8 (3)°] and there is a corresponding increase in the angle equivalent to C(9)—N(1)—C(11) of (I) [range 122.8 (3)–126.0 (2)°]. Furthermore, the angle about the C atom of the *anti*-carbonyl group subtended by the N atom and the methyl C atom [N(1)—C(11)—C(12) in (I)] is also tighter than expected [range 116.0 (3)–118.7 (4)°]. The net effect of this is that the *syn*-carbonyl and *syn*-methyl groups are positioned closer to the aryl ring [C(1)···O(1) 2.616 (4) and C(1)···C(12) 2.794 (5) Å in (I)], whereby the steric strain in the O(2)···C(10) interaction is relieved [O(2)···C(10) 2.735 (5) Å].

Experimental

Treatment of 2,5-dimethyl-6-nitroaniline with acetic anhydride and pyridine at 373 K overnight gave (I) in 78% yield. Crystals were obtained from an ethyl acetate/hexane solution.

Crystal data

$C_{12}H_{14}N_2O_4$
$M_r = 250.25$
Orthorhombic
$P2_12_12_1$
$a = 12.231\ (2)$ Å
$b = 13.643\ (3)$ Å
$c = 7.733\ (3)$ Å
$V = 1290.3\ (5)$ Å^3
$Z = 4$
$D_x = 1.288$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 19 reflections
$\theta = 9.2$–$12.1°$
$\mu = 0.098$ mm^{-1}
$T = 295$ K
Needle
0.60 × 0.20 × 0.05 mm
Colourless

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2500 measured reflections
2291 independent reflections
1650 reflections with $I > 0.5\sigma(I)$

$R_{\rm int} = 0.026$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 16$
$l = -9 \rightarrow 9$
3 standard reflections every 150 reflections intensity decay: 5.97%

Refinement

Refinement on F
$R = 0.0682$
$wR = 0.0456$
$S = 1.200$
1650 reflections
164 parameters
H atoms not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\rm max} = 0.0002$

$\Delta\rho_{\rm max} = 0.25$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.37$ e Å^{-3}
Extinction correction: Zachariasen type 2 Gaussian isotropic
Extinction coefficient: $3.0\ (3) \times 10^{-6}$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

O(1)—C(9)	1.195 (4)	N(1)—C(11)	1.414 (4)
O(2)—C(11)	1.197 (4)	N(2)—C(6)	1.470 (4)
O(3)—N(2)	1.209 (4)	C(1)—C(2)	1.387 (4)
O(4)—N(2)	1.209 (4)	C(1)—C(6)	1.392 (4)
N(1)—C(1)	1.446 (4)	C(9)—C(10)	1.497 (5)
N(1)—C(9)	1.400 (4)	C(11)—C(12)	1.485 (5)
C(1)—N(1)—C(9)	115.6 (3)	C(3)—C(4)—C(5)	121.9 (3)
C(1)—N(1)—C(11)	118.9 (3)	C(4)—C(5)—C(6)	115.6 (3)
C(9)—N(1)—C(11)	125.4 (3)	N(2)—C(6)—C(1)	117.8 (3)
O(3)—N(2)—O(4)	123.8 (3)	N(2)—C(6)—C(5)	118.8 (3)
O(3)—N(2)—C(6)	117.9 (3)	C(1)—C(6)—C(5)	123.3 (3)
O(4)—N(2)—C(6)	118.3 (3)	O(1)—C(9)—N(1)	118.9 (3)
N(1)—C(1)—C(2)	119.4 (3)	O(1)—C(9)—C(10)	120.5 (3)
N(1)—C(1)—C(6)	120.9 (3)	N(1)—C(9)—C(10)	120.5 (3)
C(2)—C(1)—C(6)	119.7 (3)	O(2)—C(11)—N(1)	121.3 (3)
C(1)—C(2)—C(3)	117.1 (3)	O(2)—C(11)—C(12)	122.5 (3)
C(2)—C(3)—C(4)	122.3 (4)	N(1)—C(11)—C(12)	116.2 (3)
C(2)—C(1)—N(1)—C(9)	−104.0 (4)		
C(2)—C(1)—N(1)—C(11)	77.9 (4)		
C(10)—C(9)—N(1)—C(11)	1.5 (5)		
O(1)—C(9)—N(1)—C(11)	−179.7 (3)		
O(2)—C(11)—N(1)—C(9)	18.0 (5)		
C(9)—N(1)—C(11)—C(12)	−162.1 (3)		
O(3)—N(2)—C(6)—C(1)	−122.7 (4)		
O(4)—N(2)—C(6)—C(1)	57.0 (4)		

Compound (I) suffered a loss of crystallinity on cutting and this necessitated the use of a large acicular sample. Data were corrected for linear decay effects. H atoms were placed in calculated positions with a C—H distance of 0.96 Å and $U_{\rm iso}$ values 1.2 times the $U_{\rm eq}$ values of the ridden atoms. Methyl-group orientations were derived from a difference synthesis.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1985). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *SIR* (Burla *et al.*, 1989). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Financial support from Proteus Molecular Design Ltd is gratefully acknowledged.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1426). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.

Beagley, B., Flowers, W. T., Hafees, A. & Pritchard, R. G. (1987). *Acta Cryst.* C**43**, 1971–1973.

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.

Domenicano, A. (1992). *Accurate Molecular Structures. Their Determination and Importance*, edited by A. Domenicano & I. Hargittai, pp. 449–463. Oxford Science Publications.

Irving, A. & Irving, H. M. N. H. (1989). *J. Cryst. Spectrosc.* **19**, 175–182.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.

Molecular Structure Corporation (1985). *MSC/AFC Diffractometer Control Software*. MSC, Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1993). *TEXSAN. Crystal Structure Analysis Package*. Version 1.6. MSC, Research Forest Drive, The Woodlands, TX 77381, USA.

Reboul, J. P., Pepe, G., Siri, D., Odden, Y., Rahal, H., Soyfer, J. C. & Barbe, J. (1992). *Acta Cryst.* C**48**, 111–115.

Reboul, J. P., Rahal, H., Pepe, G., Odden, Y., Siri, D., Astier, J. P., Soyfer, J. C. & Barbe, J. (1992). *Acta Cryst.* C**48**, 2157–2160.

Sotomatsu, T., Shigemura, M., Murata, Y. & Fujita, T. (1993). *J. Pharm. Sci.* **82**, 776–781.

Suzuki, H., Ishibashi, T., Murashima, T. & Tsukamoto, K. (1991). *Tetrahedron Lett.* **32**, 6591–6594.

Wieckowski, T. & Krygowski, T. M. (1981). *Can. J. Chem.* **59**, 1622–1629.

Acta Cryst. (1997). C**53**, 746–748

4-Cyclohexanespiro{3-[2-methoxy-2-(2,6-dimethoxyphenyl)ethenyl]oxetan-2-one}†

ALAN R. KENNEDY, WILLIAM J. KERR AND SHARON MCKENDRY

Department of Pure & Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, Scotland. E-mail: a.r.kennedy@ccsun.strath.ac.uk

(*Received 23 August 1996; accepted 27 January 1997*)

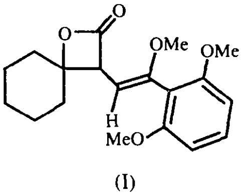
Abstract

A new and efficient route for the preparation of substituted β-lactones from chromium–carbene complexes gave the title complex, $C_{19}H_{24}O_5$, as the major stereoisomeric product.

Comment

Recently, we have discovered (Harrity, Kerr, Middlemiss & Scott, 1997) and subsequently developed (Harrity, Heron, Kerr, McKendry, Middlemiss & Scott, 1996) the reaction of α,β-unsaturated chromium–carbene complexes with propargylic alcohols to provide efficient methods for the synthesis of highly functionalized β-lactones. This entirely novel β-lactonization process further extends the use of chromium–carbene complexes in organic synthesis and, in turn, provides good to high yielding routes to this biologically important molecular sub-unit which, by our protocols, contains the synthetically attractive and highly flexible enol–ether moiety.

4-Cyclohexanespiro{3-[2-methoxy-2-(2,6-dimethoxyphenyl)ethenyl]oxetan-2-one} was prepared in 74% yield, as a 3:1 mixture of *Z* and *E* isomers, on refluxing a THF solution of pentacarbonyl[methoxy(2,6-dimethoxyphenyl)methylene]chromium(0) with an excess of 1-ethynyl-1-cyclohexanol in the presence of triethylamine and acetic anhydride. The original stereochemical assignment of the enol–ether geometry was based on ^{1}H NMR spectroscopy and NOESY studies of the mixed product and the analogous ethoxy species, 4-cyclohexanespiro{3-[2-ethoxy-2-(dimethoxyphenyl)ethenyl]oxetan-2-one}, which indicated that the major component was the *Z* isomer, (I), around the double bond. Slow recrystallization of the product from petroleum ether (303–313 K) allowed isolation of the major component (correlated by ^{1}H NMR studies) and X-ray analysis was undertaken in order to confirm that it was indeed the *Z* isomer. Subsequent ^{1}H NMR studies, supported by this structure elucidation, correlated this species with the major isomer from other lactonizations and established a more routine diagnostic process for the NMR-shift-based identification of the enol–ether isomers.



(I)

The molecular structure shown in Fig. 1 contains a near planar β-lactone four-membered ring system with a typical shortening of the O(1)—C(8) distance [O(1)—C(8) 1.351 (3) Å and O(1)—C(1) 1.504 (3) Å; see Table 1] due to the conjugation effect. The geometrical constraints of the four-membered ring leads

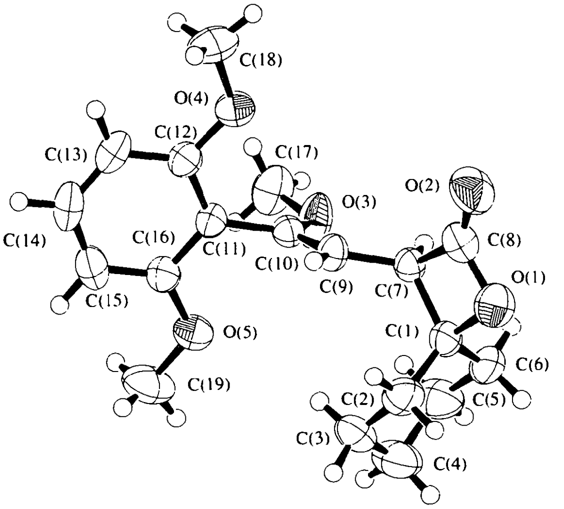


Fig. 1. *ORTEP*II (Johnson, 1976) view of compound (I). Non-H atoms are shown as 50% probability ellipsoids and H atoms are shown as small spheres of arbitrary radii.

---

† Alternative name: 3-[(*Z*)-2-methoxy-2-(2,6-dimethoxyphenyl)ethenyl]-1-oxaspiro[3.5]nonan-2-one.