

Structures of the Isomeric Triazene 1-Oxides 3-(4-Ethoxycarbonylphenyl)-1-methyltriazene 1-Oxide (1) and 3-(2-Ethoxycarbonylphenyl)-1-methyltriazene 1-Oxide (2)

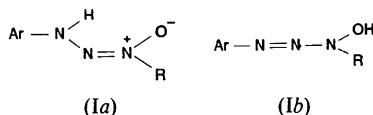
BY KEITH VAUGHAN,* LYNN M. CAMERON, SEAN CHRISTIE AND MICHAEL J. ZAWOROTKO

Department of Chemistry, Saint Mary's University, Halifax, Nova Scotia, Canada B3H 3C3

(Received 4 December 1991; accepted 18 March 1992)

Abstract. 3-(4-Ethoxycarbonylphenyl)-1-methyltriazene 1-oxide (1), $C_{10}H_{13}N_3O_3$, $M_r = 223.2$, monoclinic, $P2_1/c$, $a = 5.5055$ (13), $b = 25.2007$ (25), $c = 8.1241$ (19) Å, $\beta = 100.434$ (11)°, $V = 1108.5$ Å³, $Z = 4$, $D_x = 1.34$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.70926$ Å, $\mu = 0.9$ cm⁻¹, $F(000) = 472$, $T = 290$ K, $R = 0.044$ for 1080 unique observed reflections. 3-(2-Ethoxycarbonylphenyl)-1-methyltriazene 1-oxide (2), $C_{10}H_{13}N_3O_3$, $M_r = 223.2$, monoclinic, $P2_1/c$, $a = 12.963$ (9), $b = 8.1716$ (8), $c = 11.212$ (7) Å, $\beta = 110.85$ (3)°, $V = 1109.9$ Å³, $Z = 4$, $D_x = 1.34$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.70926$ Å, $\mu = 0.9$ cm⁻¹, $F(000) = 472$, $T = 290$ K, $R = 0.070$ for 1192 unique observed reflections. Both structures adopt the *N*-oxide tautomeric form which is in agreement with spectroscopic evidence and previously reported crystal structures of 3-(4-carbamoylphenyl)triazene 1-oxides.

Introduction. 3-Aryl-1-alkyltriazene 1-oxides (1a) are commonly synthesized by the reaction of an aryldiazonium salt with *N*-methylhydroxylamine (Miesel, 1976) and were originally described as 1-aryl-3-hydroxy-3-methyltriazenes (1b).

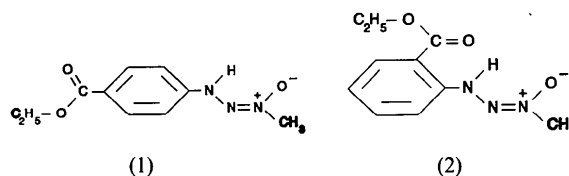


Infrared (Mitsuhashi, Osamura & Shimamura, 1965) and ¹H and ¹³C NMR data (Giumanini, Lasciani, Nisi, Petric & Stanovnik, 1983) suggested that the structure is better described as the 3-aryl-1-methyltriazene 1-oxide (1a). The 1-oxide structure has been established exclusively by the X-ray structure of 3-(4-carbamoylphenyl)-1-methyltriazene 1-oxide (Kuroda & Wilman, 1985) and several 3-aryl-1-aryltriazene 1-oxides (Samanta, De, Sarkar, Saha & Talapatra, 1985).

Additional interest in these triazene 1-oxides stems from their observed antitumour activity against the

TLX5 lymphoma and the AdjPC6/A plasmacytoma (Wilman, 1985) and the suggestion that a triazene 1-oxide may be implicated in the metabolism of the antitumour 1-aryl-3,3-dimethyltriazenes (Vaughan & Wilman, 1991).

The tautomerism of (1a) and (1b) bears some resemblance to the tautomerism exhibited by 1-aryl-3-methyltriazenes ('monomethyltriazenes'): $\text{ArN}=\text{NNHR} \rightleftharpoons \text{ArNHN}=\text{NR}$. The monomethyltriazene tautomerism has been shown to be strongly influenced by the presence of electron-withdrawing groups in the *ortho* and *para* positions of the aryl group (Hooper & Vaughan, 1981; Vaughan, 1977). Accordingly we have undertaken to investigate the structures of some triazene 1-oxides with substituent variation in the aryl group, and in this paper we report a comparison of the structures of the isomers 3-(4-ethoxycarbonylphenyl)-1-methyltriazene 1-oxide (1) and 3-(2-ethoxycarbonylphenyl)-1-methyltriazene 1-oxide (2).



Experimental. Compounds (1) and (2) were synthesized by coupling the appropriate aryldiazonium salt with *N*-methylhydroxylamine, according to the method of Miesel (1976): (1) 80% yield, m.p. 422–425 K (from ethyl acetate); (2) 56% yield, m.p. 394–395 K (from toluene). NMR and IR spectra and elemental analysis (C,H,N) confirmed the assigned structures.

Single crystals of (1) and (2) were independently mounted and sealed in separate glass capillaries and were then optically centred in the X-ray beam on an Enraf-Nonius CAD-4 automated diffractometer. The structures were solved by direct methods and refined using full-matrix least-squares techniques. Ring H atoms and methylene H atoms were placed

* Author to whom correspondence should be addressed.

Table 1. Summary of intensity-data collection and structure refinement

	(1)	(2)
Colour	Yellow	Yellow
Maximum crystal dimensions (mm)	0.15 × 0.30 × 0.60	0.65 × 0.72 × 1.35
Scan type	$\omega/2\theta$	$\omega/2\theta$
Radiation	Mo K α	Mo K α
Scan width (°)	0.80 + 0.35tan θ	0.90 + 0.35tan θ
Transmission range	0.816, 0.977	0.579, 0.977
Decay of standards (%)	± 2	± 2
No. of reflections used for unit-cell determination*	24	24
No. of reflections measured	1611	1513
2 θ range (°)	2–45	2–45
Range of <i>h</i> , <i>k</i> , <i>l</i>	–5, 5; 0, 27; 0, 8	–13, 13; 0, 8; 0, 12
No. of unique reflections	1445	1440
No. of reflections observed†	1080	1192
Computer programs‡	NRCVAX§	NRCVAX§
Structure solution	Direct	Direct
No. of parameters	149	149
Weight modifier, <i>k</i>	0.00001	0.00002
GOF	3.87	8.58
<i>R</i>	0.044	0.070
<i>wR</i>	0.043	0.083
Final difference map maximum (e Å ⁻³)	0.13	0.38
Maximum $\Delta\sigma$	0.000	0.000

* Least-squares refinement of $[(\sin\theta)/\lambda]^2$ for 24 reflections with $\theta > 18^\circ$ for (1) and $\theta > 14.5^\circ$ for (2).

† $I > 2.5\sigma(I)$ for (1) and $I > 3.0\sigma(I)$ for (2). Corrections: Lorentz-polarization and absorption (empirical ψ scan).

‡ Neutral scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV).

§ An interactive program system for structure analysis (Gabe, Le Page, Charland, Lee & White, 1989).

in calculated positions (C—H = 1.08 Å) and assigned isotropic temperature factors equivalent to those calculated for the C atom to which they are bonded. Methyl H atoms and the H atom bonded to the N atom were located *via* inspection of difference Fourier maps and were fixed to the attached C atoms. Only the H atoms bonded to N atoms were subsequently refined. Final values of *R* and *wR* [$w^{-1} = \sigma^2(F_o) + kF_o^2$] are given with other pertinent data-collection and structure-refinement parameters in Table 1.* Final fractional coordinates and equivalent isotropic thermal parameters for non-H atoms are given in Table 2 for (1) and (2).

Discussion. The molecular structure of (1) is shown in Fig. 1, that of (2) in Fig. 2. Table 3 lists molecular geometry for (1) and (2). The results show that both molecules adopt the *N*-oxide tautomeric form (1a) in agreement with the spectroscopic evidence and the previously reported crystal structures of similar compounds. In both molecules, the N(2)—N(3) bond is shorter than the N(1)—N(2) bond by *ca* 0.08 Å.

The structure of compound (1), illustrated by an ORTEP (Johnson, 1965) view in Fig. 1, shows that the four atoms of the triazene *N*-oxide group, N(1)—

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, complete geometry and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55305 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR0018]

Table 2. Atomic parameters and equivalent isotropic thermal parameters (Å²) for (1) and (2)

<i>B</i> _{eq} is the mean of the principal axes of the thermal ellipsoid.				
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
(1)				
O(1)	0.8705 (4)	0.85919 (9)	1.7009 (3)	4.70 (13)
O(2)	1.1266 (4)	0.81044 (9)	1.5749 (3)	4.64 (12)
O(3)	0.3164 (4)	0.94548 (9)	0.6393 (3)	5.16 (12)
N(1)	0.5085 (5)	0.91827 (1)	0.9296 (3)	3.91 (15)
N(2)	0.2988 (5)	0.94732 (10)	0.9143 (3)	3.66 (13)
N(3)	0.2159 (5)	0.95955 (10)	0.7617 (3)	3.56 (13)
C(1)	0.6133 (6)	0.90004 (12)	1.0883 (4)	3.30 (15)
C(2)	0.5079 (6)	0.91192 (12)	1.2270 (4)	3.78 (16)
C(3)	0.6180 (6)	0.89372 (13)	1.3832 (4)	3.82 (16)
C(4)	0.8328 (6)	0.86365 (12)	1.4042 (4)	3.20 (15)
C(5)	0.9361 (6)	0.85196 (12)	1.2643 (4)	3.50 (15)
C(6)	0.8284 (6)	0.87000 (13)	1.1068 (4)	3.64 (15)
C(7)	0.9410 (6)	0.84557 (13)	1.5742 (4)	3.76 (17)
C(8)	1.2418 (7)	0.79028 (13)	1.7382 (4)	5.18 (19)
C(9)	1.4411 (6)	0.75254 (16)	1.7085 (5)	6.10 (21)
C(10)	–0.0118 (6)	0.99109 (13)	0.7298 (4)	3.95 (16)
(2)				
O(1)	0.2219 (3)	0.2816 (4)	0.0465 (3)	4.84 (18)
O(2)	0.12564 (23)	0.4226 (3)	0.1419 (3)	4.30 (16)
O(3)	0.3886 (3)	0.1864 (4)	–0.1478 (3)	5.62 (21)
N(1)	0.3304 (3)	0.4431 (4)	–0.0754 (3)	4.08 (20)
N(2)	0.3930 (3)	0.4598 (4)	–0.1478 (3)	3.78 (19)
N(3)	0.4181 (3)	0.3233 (4)	–0.1811 (3)	3.68 (19)
C(1)	0.2932 (3)	0.5882 (5)	–0.0325 (4)	3.17 (20)
C(2)	0.2271 (3)	0.5752 (5)	0.0424 (4)	3.20 (21)
C(3)	0.1930 (4)	0.7150 (5)	0.0858 (4)	4.07 (23)
C(4)	0.2203 (4)	0.8699 (5)	0.0531 (4)	4.47 (25)
C(5)	0.2839 (4)	0.8809 (5)	–0.0235 (4)	4.6 (3)
C(6)	0.3200 (4)	0.7401 (6)	–0.0654 (4)	4.34 (25)
C(7)	0.1939 (3)	0.4104 (5)	0.0757 (4)	3.39 (22)
C(8)	0.0889 (3)	0.2737 (6)	0.1780 (4)	4.68 (24)
C(9)	0.0202 (4)	0.3162 (6)	0.2548 (5)	5.3 (3)
C(10)	0.4831 (4)	0.3271 (5)	–0.2632 (4)	4.29 (24)

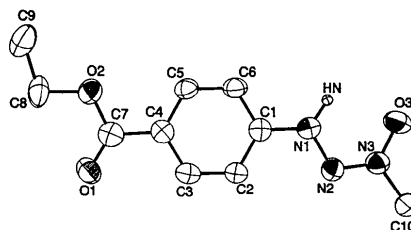


Fig. 1. Plan view of 3-(4-ethoxycarbonylphenyl)-1-methyltriazen-1-oxide (1).

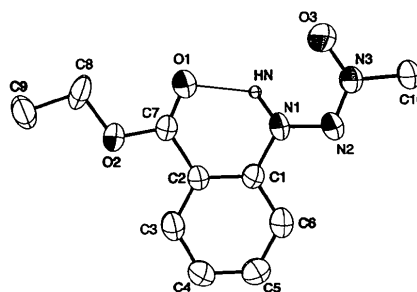


Fig. 2. Plan view of 3-(2-ethoxycarbonylphenyl)-1-methyltriazen-1-oxide (2).

N(2)—N(3)—O(3), are closely planar ($\chi^2 = 3.2$, maximum deviation = 0.004 Å). The average plane of the group forms a dihedral angle of 2.58° with the phenyl ring. Kuroda & Wilman (1985) attributed this

Table 3. *Interatomic distances (Å) and angles (°) for (1) and (2)*

	(1)	(2)
O(1)—C(7)	1.213 (4)	1.196 (5)
O(2)—C(7)	1.351 (4)	1.346 (4)
O(2)—C(8)	1.454 (4)	1.417 (5)
O(3)—N(3)	1.272 (3)	1.280 (5)
N(1)—N(2)	1.354 (4)	1.344 (4)
N(1)—C(1)	1.391 (4)	1.426 (5)
N(2)—N(3)	1.279 (4)	1.255 (5)
N(3)—C(10)	1.467 (4)	1.453 (5)
C(1)—C(2)	1.390 (4)	1.402 (5)
C(1)—C(6)	1.390 (4)	1.374 (6)
C(2)—C(3)	1.382 (4)	1.375 (6)
C(3)—C(4)	1.389 (4)	1.398 (6)
C(4)—C(5)	1.392 (4)	1.390 (6)
C(4)—C(7)	1.474 (4)	—
C(2)—C(7)	—	1.500 (5)
C(5)—C(6)	1.386 (4)	1.385 (6)
C(8)—C(9)	1.504 (5)	1.484 (6)
N(1)—H(N1)	0.94 (3)	1.07 (3)
N(1)···O(3)	2.499 (3)	—
N(1)···O(1)	—	2.636 (4)
O(3)—H(N1)	2.08 (3)	2.15 (3)
O(1)—H(N1)	—	1.80 (3)
C(7)—O(2)—C(8)	115.9 (3)	116.6 (3)
N(2)—N(1)—C(1)	117.9 (3)	117.9 (3)
N(1)—N(2)—N(3)	111.60 (24)	111.4 (3)
O(3)—N(3)—N(2)	124.1 (3)	123.6 (3)
O(3)—N(3)—C(10)	119.43 (24)	120.3 (3)
N(2)—N(3)—C(10)	116.4 (3)	116.1 (3)
N(1)—C(1)—C(2)	121.0 (3)	119.4 (3)
N(1)—C(1)—C(6)	118.8 (3)	120.9 (3)
C(2)—C(1)—C(6)	120.1 (3)	119.7 (3)
C(1)—C(2)—C(3)	119.7 (3)	119.4 (3)
C(2)—C(3)—C(4)	121.1 (3)	121.1 (3)
C(3)—C(4)—C(5)	118.7 (3)	118.8 (4)
C(3)—C(4)—C(7)	118.4 (3)	—
C(5)—C(4)—C(7)	123.0 (3)	—
C(1)—C(2)—C(7)	—	120.5 (3)
C(3)—C(2)—C(7)	—	120.1 (3)
C(4)—C(5)—C(6)	121.0 (3)	120.1 (4)
C(1)—C(6)—C(5)	119.5 (3)	120.8 (4)
O(1)—C(7)—O(2)	122.7 (3)	122.6 (3)
O(1)—C(7)—C(4)	124.8 (3)	—
O(2)—C(7)—C(4)	112.6 (3)	—
O(1)—C(7)—C(2)	—	125.5 (3)
O(2)—C(7)—C(2)	—	111.9 (3)
O(2)—C(8)—C(9)	106.6 (3)	107.3 (4)
N(1)—H(N1)—O(3)	104.5 (22)	—
O(1)—HN—N(1)	—	131.7 (22)

Table 4. *Comparison of bond lengths (Å) in the four triazene 1-oxides*

	(1)	(2)	(3)*	(4)†
N(1)—N(2)	1.353	1.344	1.340	1.383
N(2)—N(3)	1.279	1.255	1.271	1.280
N(3)—O(3)	1.270	1.280	1.284	1.259
N(3)—C(10)	1.463	1.453	1.464	1.470
N(1)—C(1)	1.390	1.426	1.403	1.405
N(1)—HN	0.94	1.07	1.05	—
O(3)—HN	2.08	2.15	—	—
C(4)—C(7)	1.474	1.500‡	1.492	1.500
C(7)—O(1)	1.214	1.196	1.250	1.368
C(7)—X	1.351	1.346	1.317	—
O(1)—HN	—	1.80	—	—

* Kuroda & Wilman (1985).

† Neidle, Webster, Kuroda & Wilman (1987).

‡ C(2)—C(7) in compound (2).

deviation in the analogous amide to repulsion between H(C6) and H(N1). The N(1) and O(3) atoms are *cis* to each other. The O(3)···H(N1) and O(3)···N contacts of 2.08 (3) and 2.499 (3) Å, respectively, are more likely to be of geometric origin than a result of N—H···O hydrogen bonding. There are no significant intermolecular contacts (Fig. 2), the

closest being between the ester carbonyl O atom, O(1), and H(N1) of another molecule (2.50 Å). The atoms of the ethoxycarbonyl group in (1) are highly planar ($\chi^2 = 3.6$, max. deviation 0.006 Å) and subtend a dihedral angle of 8.57° with the phenyl moiety.

The *ortho* isomer (2), an *ORTEP* view of which is presented in Fig. 2, is somewhat different from that of the *para* isomer (1). The most obvious difference is the strong intramolecular hydrogen bond between H(N1) and O(1) of the ester group. The H(N1)···O(1) and N···O distances of 1.80 (3) and 2.636 (4) Å, respectively, are well within the range for hydrogen bonding (Hamilton & Ibers, 1968; Joesten & Schaad, 1974). The presence of this hydrogen bond had been suggested from spectroscopy (Cameron, Hooper &

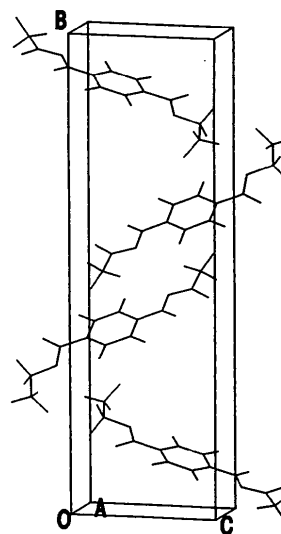


Fig. 3. Unit cell of structure (1).

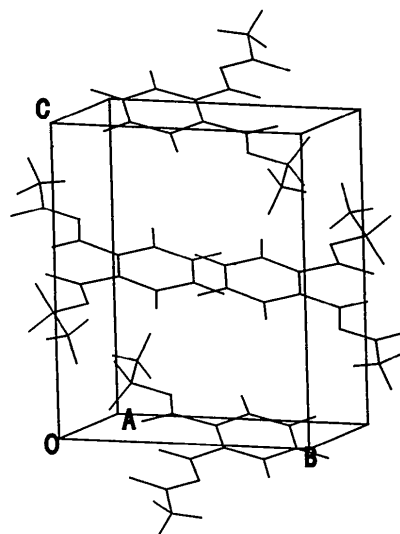
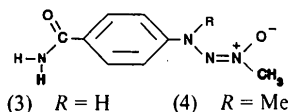


Fig. 4. Unit cell of structure (2).

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)°, $V = 1044.1$ Å³, $Z = 4$, $D_x = 1.57$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 1.2$ cm⁻¹, $F(000) = 504$, $T = 293$ 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.