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## Structure of (*Z,Z*)-*N*-{[2-(4-Methylphenyl)-2-(4-methylphenyl)imino]ethylidene}aniline *N*-Oxide: Conjugation in Systems with the Nitrono Moiety

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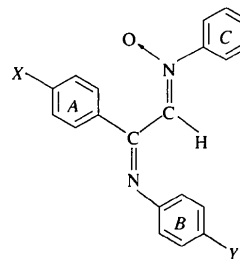
### Abstract

The crystal structure of the title compound has been determined. The crystals are orthorhombic:  $Pna2_1$ ,  $a = 8.6190(6)$ ,  $b = 10.9705(6)$ ,  $c = 18.7157(6)$  Å,  $V = 1769.7(2)$  Å<sup>3</sup>,  $Z = 4$ . The structure was solved by direct methods and refined using 2127 reflections with  $F^2 \geq 2\sigma(F^2)$  to a final  $R = 0.0371$  and  $wR(F^2) = 0.0865$ . Second-harmonic generation (SHG) activity was checked by Kurtz powder method in relation to urea. The molecule reveals the *Z,Z,s-E*-configuration of the 1,4-diazabutadiene fragment with a  $N=C-C=N$  torsion angle of  $-145.8(3)^\circ$ . All aryl rings are twisted against each other. The crystal packing is controlled by very weak  $C-H \cdots O$  hydrogen bonding, coupling of dipoles and weak van der Waals interactions. An influence of  $\pi$ -electron conjugation on the geometry of the nitrono moiety in conjugated systems  $X=C-C=N \rightarrow O$  ( $X = C, N$  or  $O$ ) is discussed.

### Introduction

This work is a continuation of the structural study of 1,2,4-triaryl-1,4-diazabutadiene *N*<sup>4</sup>-oxides (see Scheme) with different substituents *X* and *Y* in *A* and *B* phenyl rings, respectively. The presented *N*-oxide (*N22*) has methyl groups in both positions *X* and *Y*, whereas the previously described compounds had  $X = H$  and either a methoxy (*N11*) or *N,N*-dimethylamino (*N15*) group in the *Y* position (Olszewski & Stadnicka, 1995). The <sup>13</sup>C NMR spectra of nitrones having the 1,4-diazabutadiene system, in addition to the nitrono group, showed distinct upfield shifts, which indicated conjugation of the two hetero bonds and supported an almost coplanar arrangement of the azomethine and nitrono groups

(Moskal & Milart, 1985). Although the planarity of the system is necessary for full conjugation, the nitrones cannot achieve planarity due to steric hindrance between the H atoms of the aldonitrono carbon and phenyl ring *B*. Therefore, a question arises if a degree of conjugation can be related to the geometry of the  $X=C-C=N(\rightarrow O)$  fragment with  $X = C, N$  or  $O$ . To answer this question the database study was performed. The structural data of two other nitrones, *N25* and *N65*, which will be published elsewhere, are also taken into account.



- N11*  $X = H, Y = OCH_3$   
*N15*  $X = H, Y = N(CH_3)_2$   
*N22*  $X = CH_3, Y = CH_3$   
*N25*  $X = CH_3, Y = N(CH_3)_2$   
*N65*  $X = Br, Y = N(CH_3)_2$

### Experimental

The title compound was obtained according to the procedure published earlier for the other conjugated nitrones (Moskal & Milart, 1984) and purified by repeated recrystallization from saturated (at boiling point) ethanol solution. Yield 62%, m.p. 464–465 K. *Elemental analysis*. Found: C 80.32, H 6.11, N 8.62; calc.

Table 1. *Crystal data and structure refinement*

Empirical formula	C <sub>22</sub> H <sub>20</sub> N <sub>2</sub> O
Formula weight	328.40
Temperature (K)	293 (2)
Radiation, λ (Å)	Cu Kα <sub>1</sub> , 1.54056
Crystal system	Orthorhombic
Space group	<i>Pna</i> 2 <sub>1</sub>
Unit-cell dimensions	
<i>a</i> (Å)	8.6190 (6)
<i>b</i> (Å)	10.9705 (6)
<i>c</i> (Å)	18.7157 (6)
Volume (Å <sup>3</sup> )	1769.7 (2)
<i>Z</i>	4
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	1.233
Absorption coefficient (mm <sup>-1</sup> )	0.597
<i>F</i> (000)	696
Crystal size (mm)	0.15 × 0.10 × 0.05
Crystal description	Yellow plate
θ range for data collection (°)	1–73
Index ranges	0 ≤ <i>h</i> ≤ 10, –13 ≤ <i>k</i> ≤ 10, –23 ≤ <i>l</i> ≤ 23
Reflections collected*	7056, of which 3619 with <i>I</i> ≥ 2σ( <i>I</i> )
Independent reflections	2127 ( <i>R</i> <sub>int</sub> = 0.0359), <i>I</i> ≥ 2σ( <i>I</i> )
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	2127/1 (floating origin)/307
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.107
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> = 0.0371, <i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.0865
Weighting scheme	<i>w</i> = 1/[σ <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) + (0.0450 <i>P</i> ) <sup>2</sup> + 0.16 <i>P</i> ], where <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3.
Extinction coefficient	0.0017 (2)
Largest difference peak and hole (e Å <sup>-3</sup> )	0.138 and –0.112

\* The large amount of weak reflections was probably due to relatively small crystal dimensions.

for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O: C 80.44, H 6.15, N 8.53%. \* *Spectral properties.* IR (nujol),  $\bar{\nu}$ (cm<sup>-1</sup>): 1600 (C=N), 1566, 1546, 1513, 1493 (aromatic rings), 1053 (N—O). IR spectra were recorded with an IR75 Specord (Zeiss, Jena) spectrometer. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>/TMS), δ (p.p.m.): 8.32 (*s*, 1H, nitron proton), 7.82–6.90 (*m*, 13H, aromatic protons), 2.40 (*s*, 3H, methyl group in *X* position), 2.28 (*s*, 3H, methyl group in *Y* position). <sup>1</sup>H NMR spectra were recorded at 100 MHz with a Tesla BS-567A spectrometer.

Yellow plate-shaped crystals suitable for X-ray experiment were obtained from the saturated ethanol solution. The unit-cell parameters were determined and refined by least-squares for 29 reflections measured in the range 4.7 ≤ θ ≤ 29.7° using a KM-4 diffractometer [KUMA diffraction, λ(Cu Kα<sub>1</sub>) = 1.54056 Å, graphite monochromator]. The details of crystal data and intensity measurements are given in Table 1.†

The intensity data were corrected for Lorentz and polarization effects. The structure was solved by direct

\* Elemental analyses were performed in the Regional Laboratory of Physicochemical Analysis and Structural Research (Jagiellonian University, Kraków).

† Lists of observed and calculated structure factors, anisotropic displacement parameters, H-atom coordinates and the least-squares mean planes have been deposited with the IUCr (Reference: PA0301). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for non-H atoms*

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
O(1)	0.0769 (3)	0.7252 (2)	0.5778 (1)	0.056 (1)
N(1)	0.1728 (3)	0.7230 (2)	0.3673 (1)	0.049 (1)
N(2)	0.1769 (3)	0.6493 (2)	0.5523 (1)	0.040 (1)
C(1)	0.1869 (3)	0.8781 (3)	0.4553 (2)	0.041 (1)
C(2)	0.2704 (4)	0.9216 (3)	0.5138 (2)	0.044 (1)
C(3)	0.2714 (4)	1.0445 (3)	0.5285 (2)	0.052 (1)
C(4)	0.1891 (4)	1.1274 (3)	0.4877 (2)	0.053 (1)
C(5)	0.1041 (5)	1.0826 (3)	0.4306 (2)	0.058 (1)
C(6)	0.1037 (4)	0.9602 (3)	0.4141 (2)	0.050 (1)
C(7)	0.1891 (4)	0.7474 (3)	0.4345 (2)	0.043 (1)
C(8)	0.1649 (4)	0.6007 (3)	0.3420 (1)	0.042 (1)
C(9)	0.0559 (4)	0.5183 (3)	0.3651 (2)	0.051 (1)
C(10)	0.0456 (5)	0.4032 (3)	0.3336 (2)	0.055 (1)
C(11)	0.1451 (4)	0.3692 (3)	0.2794 (2)	0.052 (1)
C(12)	0.2535 (4)	0.4534 (3)	0.2565 (2)	0.053 (1)
C(13)	0.2628 (4)	0.5680 (3)	0.2862 (2)	0.050 (1)
C(14)	0.2280 (4)	0.6513 (3)	0.4863 (2)	0.043 (1)
C(15)	0.2301 (3)	0.5543 (2)	0.6010 (2)	0.039 (1)
C(16)	0.3818 (4)	0.5138 (3)	0.5984 (2)	0.045 (1)
C(17)	0.4282 (5)	0.4235 (3)	0.6460 (2)	0.056 (1)
C(18)	0.3240 (5)	0.3777 (4)	0.6957 (2)	0.062 (1)
C(19)	0.1752 (5)	0.4204 (4)	0.6977 (2)	0.062 (1)
C(20)	0.1255 (4)	0.5091 (3)	0.6505 (2)	0.050 (1)
C(21)	0.1900 (9)	1.2623 (4)	0.5055 (3)	0.086 (2)
C(22)	0.1333 (8)	0.2445 (4)	0.2448 (3)	0.078 (1)

methods using *SHELXS86* (Sheldrick, 1985) in the space group *Pna*2<sub>1</sub>. Full-matrix least-squares anisotropic refinement on *F*<sup>2</sup> was performed with *SHELXL93* (Sheldrick, 1993). All H atoms were found from subsequent difference Fourier syntheses and refined with isotropic temperature parameters.

The refinement converged at *R* = 0.0371 and *wR*(*F*<sup>2</sup>) = 0.0865. The maximum shift-to-standard deviation ratio in the last cycle was 0.003 for *z* H(223). Weighting scheme: *w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (0.0450*P*)<sup>2</sup> + 0.164*P*], where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3 was used.

Non-linear optic properties (NLO) of *N*22 were estimated qualitatively using a type of Kurtz powder test.\* The relative harmonic intensity for second-harmonic generation (SHG) was found to be 0.10 against the urea standard at 1064 nm using a Nd:YAG laser.

### Structural results

Final positional parameters with equivalent thermal displacement parameters are listed in Table 2, while bond lengths, angles and selected torsion angles of non-H atoms are given in Table 3. The molecular structure with the numbering scheme is shown in Fig. 1.

Presented nitron has the same *Z,Z,s-E* configuration of the 1,4-diazabutadiene moiety as previously described, *N*11 and *N*15. The N(1)—C(7)—C(14)—N(2) fragment is not planar with the appropriate torsion angle –145.8(3)°, and bond lengths are in agreement, within the limit of error, with the values found for *N*11 and *N*15

\* The experiment was performed at the Inorganic Chemistry Laboratory, Oxford University, and will be described elsewhere.

Table 3. Bond lengths (Å) and angles (°) for non-H atoms and selected torsion angles (°) with e.s.d.'s in parentheses

C(1)—C(6)	1.386 (4)	C(10)—C(11)	1.380 (5)
C(1)—C(2)	1.394 (4)	C(11)—C(12)	1.382 (5)
C(1)—C(7)	1.486 (4)	C(11)—C(22)	1.516 (5)
C(2)—C(3)	1.376 (5)	C(12)—C(13)	1.378 (5)
C(3)—C(4)	1.384 (5)	C(14)—N(2)	1.312 (4)
C(4)—C(5)	1.385 (5)	N(2)—O(1)	1.290 (3)
C(4)—C(21)	1.517 (5)	N(2)—C(15)	1.458 (4)
C(5)—C(6)	1.377 (5)	C(15)—C(16)	1.382 (4)
C(7)—N(1)	1.293 (3)	C(15)—C(20)	1.384 (4)
C(7)—C(14)	1.470 (4)	C(16)—C(17)	1.391 (4)
N(1)—C(8)	1.424 (4)	C(17)—C(18)	1.387 (5)
C(8)—C(9)	1.373 (5)	C(18)—C(19)	1.365 (6)
C(8)—C(13)	1.390 (4)	C(19)—C(20)	1.382 (5)
C(9)—C(10)	1.397 (5)		
C(6)—C(1)—C(2)	118.7 (3)	C(11)—C(10)—C(9)	121.0 (4)
C(6)—C(1)—C(7)	119.2 (3)	C(10)—C(11)—C(12)	117.9 (3)
C(2)—C(1)—C(7)	122.0 (3)	C(10)—C(11)—C(22)	121.0 (4)
C(3)—C(2)—C(1)	119.8 (3)	C(12)—C(11)—C(22)	121.1 (4)
C(2)—C(3)—C(4)	122.0 (3)	C(13)—C(12)—C(11)	121.6 (3)
C(3)—C(4)—C(5)	117.7 (3)	C(12)—C(13)—C(8)	120.2 (4)
C(3)—C(4)—C(21)	121.1 (4)	N(2)—C(14)—C(7)	123.8 (2)
C(5)—C(4)—C(21)	121.2 (4)	O(1)—N(2)—C(14)	124.2 (2)
C(6)—C(5)—C(4)	121.3 (3)	O(1)—N(2)—C(15)	116.2 (2)
C(5)—C(6)—C(1)	120.5 (3)	C(14)—N(2)—C(15)	119.6 (2)
N(1)—C(7)—C(14)	121.2 (3)	C(16)—C(15)—C(20)	121.6 (3)
N(1)—C(7)—C(1)	116.9 (3)	C(16)—C(15)—N(2)	120.4 (3)
C(14)—C(7)—C(1)	121.5 (3)	C(20)—C(15)—N(2)	118.0 (3)
C(7)—N(1)—C(8)	121.5 (2)	C(15)—C(16)—C(17)	118.6 (3)
C(9)—C(8)—C(13)	118.8 (3)	C(18)—C(17)—C(16)	120.1 (4)
C(9)—C(8)—N(1)	123.2 (3)	C(19)—C(18)—C(17)	120.1 (3)
C(13)—C(8)—N(1)	117.6 (3)	C(18)—C(19)—C(20)	121.0 (4)
C(8)—C(9)—C(10)	120.4 (3)	C(19)—C(20)—C(15)	118.5 (3)
C(6)—C(1)—C(7)—N(1)	28.4 (5)		
C(2)—C(1)—C(7)—C(14)	23.0 (5)		
C(14)—C(7)—N(1)—C(8)	11.0 (5)		
C(1)—C(7)—N(1)—C(8)	-176.6 (3)		
C(7)—N(1)—C(8)—C(9)	57.6 (5)		
C(7)—N(1)—C(8)—C(13)	-129.0 (3)		
N(1)—C(8)—C(13)—C(12)	-175.8 (3)		
N(1)—C(8)—C(9)—C(10)	174.2 (3)		
N(1)—C(7)—C(14)—N(2)	-145.8 (3)		
C(1)—C(7)—C(14)—N(2)	42.2 (5)		
C(7)—C(14)—N(2)—O(1)	6.0 (5)		
C(7)—C(14)—N(2)—C(15)	-176.1 (3)		
O(1)—N(2)—C(15)—C(16)	-144.4 (3)		
C(14)—N(2)—C(15)—C(16)	37.5 (4)		
C(14)—N(2)—C(15)—C(20)	-144.2 (3)		
O(1)—N(2)—C(15)—C(20)	33.9 (4)		

(cf.  $C''=X$ ,  $C''-C$  and  $C=N$  lengths in Table 5). A decrease of conjugation between  $\pi$ -electrons of double bonds as expected for the observed non-planarity results in the bond length 1.470(4) Å for C(7)—C(14). The value is close to the average  $Csp^2-Csp^2$  distance observed for unconjugated butadienes [1.478(12) Å], whereas for conjugated structures its typical value is 1.455(11) Å (Allen *et al.*, 1987). N(1)—C(7) and N(2)—C(14) double bonds of 1.293(3) and 1.312(4) Å, respectively, are slightly elongated when compared with the average  $N=C$  value for the  $C(ar)-C=N-C$  fragment [1.279(8) Å; Allen *et al.*, 1987]. The additional elongation of the N(2)—C(14) bond is due to the presence of the strongly electro-negative O(1) atom of the nitrone group. The

N(2)—O(1) bond length of N22 does not differ from the values found for N11 [1.295(2) Å] and N15 [1.290(3) Å] and, as in all these structures, the O(1)—N(2)—C(15) angle is significantly smaller than 120°.

The whole molecule cannot achieve a planar conformation mainly because of the steric hindrance between H atoms at C(14) and C(9), as well as between O(1) and the H atom at C(2), although the shortest observed non-bonding intramolecular distances are larger than the sum of the inappropriate van der Waals radii [ $H(14)\cdots H(9)$  3.10(5),  $H(2)\cdots O(1)$  2.74(3) Å].

All aryl rings, *A*, *B* and *C*, are twisted against each other:  $\angle A, B = 85.33(8)$ ,  $\angle B, C = 68.54(10)$  and  $\angle A, C = 85.53(10)^\circ$ . The angle  $60.71(11)^\circ$  between ring *B* and the mean N(1), C(7), C(14), C(1) plane is greater than those observed for the other studied nitrones of the 1,4-diazabutadiene system [N11: 48.7(1); N15: 48.4(1)°].

The packing of N22 is shown in Fig. 2. Molecules form columns parallel to the *a* direction due to weak hydrogen bonding [ $C(2)-H(2)\cdots O(1)$  ( $x + \frac{1}{2}, -y + \frac{3}{2}, z$ ); 3.318(4), 2.42(3) Å, 152(3)°]. The shortest  $H\cdots H$  contact, 2.48(5) Å, is found between H(3) and H(20) ( $x + \frac{1}{2}, -y + \frac{3}{2}, z$ ) within the column. The columns

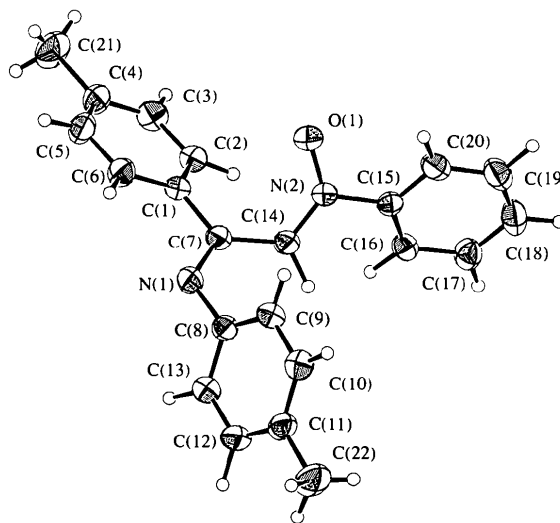


Fig. 1. ORTEP (Johnson, 1976) view of N22 molecule with thermal ellipsoids at the 40% probability level.

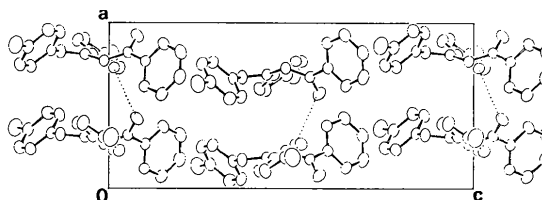


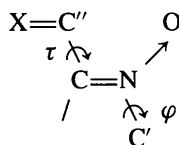
Fig. 2. Packing diagram of N22 projected onto the *ac* plane. Only non-H atoms are shown. The possible hydrogen bond  $C(2)-H(2)\cdots O(1)$  ( $x + \frac{1}{2}, -y + \frac{3}{2}, z$ ) is marked by dotted lines.

are held together by attraction of the almost antiparallel dipoles.

It is interesting to compare the packing of *N22* and the centrosymmetric structure of *N15* [space group *Pbca*,  $a = 8.989(3)$ ,  $b = 9.6878(11)$ ,  $c = 41.670(4)$  Å]. In *N22*, benzene ring *C* is oriented towards the methyl substituent of ring *B* of the neighbouring molecule ('head-to-tail' arrangement) giving a periodicity of  $c = 18.7157(6)$  Å. In *N15* the *c* period is more than doubled due to the 'head-to-head' arrangement of the molecules which are oriented with their *Y* substituent towards each other [ $Y = \text{N}(\text{CH}_3)_2$ ]. It can be noticed that the packing is determined by the lipophilic and hydrophilic character of the peripheral groups, which come close to each other when of the same character.

### Database study

The enlargement of the  $\text{C}=\text{N}\rightarrow\text{O}$  bond system in *N*-oxides through an additional double bond or aromatic system attached to a C atom (so called conjugated nitrones)



seems to have an influence on the geometry of this fragment.

To analyse this the Cambridge Structural Database (CSD, 1993) has been searched. To prevent any atom of the fragment being connected by a cyclic bond to an atom outside the fragment, the *NOCR* option in the *QUEST88* (Allen *et al.*, 1991) program was used. Among 26 structures retrieved from the CSD and containing the  $\text{C}=\text{N}(\rightarrow\text{O})-\text{C}'$  moiety, 22 structures were found to contain the enlarged system  $\text{X}=\text{C}''-\text{C}=\text{N}(\rightarrow\text{O})-\text{C}'$ , with  $\text{X} = \text{C}$  or  $\text{O}$ . Table 4 lists the refcodes and bibliographic information for the resulting structures. The title compound, as well as the other conjugated nitrones of the 1,4-diazabutadiene system (see previous Scheme), appeared to be the only structures with  $\text{X} = \text{N}$ . A total number of 31 structures (35 independent molecules) was taken for further analysis from the point of view of the selected geometrical parameters given in Table 5. Bond lengths, valence angles and torsion angles inspection showed several interesting relationships, as discussed below.

The  $\text{C}=\text{N}(\rightarrow\text{O})-\text{C}'$  fragment is planar with the  $\text{C}'-\text{N}\rightarrow\text{O}$  angle of mean value  $114.7(2)^\circ$  significantly smaller than the  $120^\circ$  expected for  $\text{N}sp^2$  hybridization.  $\text{C}=\text{N}-\text{C}'$  and  $\text{C}=\text{N}\rightarrow\text{O}$  angles are distinctly correlated to each other (correlation coefficient =  $-0.829$ ,  $R^2 = 69\%$ ).

The correlations of  $\text{C}=\text{N}$ ,  $\text{C}''-\text{C}$  and  $\text{N}\rightarrow\text{O}$  bond lengths against the torsion angle  $\tau = \text{X}-\text{C}''-\text{C}-\text{N}$  are observed for the conjugated nitrones (Fig. 3), and  $\tau$

Table 4. List of compounds in this study and their bibliographic references

AMCBAO:	Jensen & Jerslev (1969).
BOWZES:	Inouye (1983).
CASTEV:	Lobo, Prabhakar, Rzepa, Skapski, Tavares & Widdowson (1983).
CEJVUI:	Inouye (1984).
CINZII:	Wovkulich, Barcelos, Batcho, Sereno, Baggolini, Hennessy & Uskokovic (1984).
CIPWED:	Greci & Sgarabotto (1984).
DAPXOH:	Kliegel, Preu, Rettig & Trotter (1985).
DEDWEO:	Falshaw, Hashi & Taylor (1985).
DIYRIM:	Huber, Knierzinger, Obrecht & Vasella (1985).
ETCBPO:	Penning, Reinhoudt, Harkema & Vanhummel (1980).
FAHYUI:	Coates & Firsan (1986).
FEXBOZ:	Liu, Wang, Chen & Xu (1987).
GASGAI:	Sweeny & Singh (1988).
JIBFAB:	Pritchard, Banks, Duboisson & Tipping (1991).
KAMIAJ:	Carroll, Mullen & Georgiev (1989).
KESNEB:	Liu, Wang, Liu & Xu (1990).
KUJBEW:	Branco, Prabhakar, Lobo & Williams (1992).
MCBZOZ:	Folting, Lipscomb & Jerslev (1964).
MXIDPO:	Romers & Hesper (1966).
SADHOU:	Boyd, Boyd, Burnett, Malone & Jennings (1988).
TAFRUN:	Christensen, Jorgensen & Hazell (1990).
TPNITR:	Brown & Trefonas (1973).
TPNITR01:	Falshaw, Hashi & Taylor (1985).
VAXFUV:	Toda, Tanaka & Mak (1989).
VIRJIP:	Deshong, Wei, Kennington, Ammon & Leginus (1991).
VIVVOL:	Ganazzoli, Dalpozzo & Grossi (1991).

can be considered as a measure of the system deviation from planarity. The full conjugation is possible in the case of  $\tau = 0$  (*s-Z* conformation) or  $\tau = 180^\circ$  (*s-E* conformation), whereas for  $\tau = 90$  or  $270^\circ$  lack of conjugation is expected.

It was noticed that those molecules in which the  $\text{N}\rightarrow\text{O}$  group is involved as an acceptor in strong intra- or intermolecular hydrogen bonding have a remarkably lengthened  $\text{N}-\text{O}$  bond, and they do not obey the above relationship. Such molecules (five cases) were excluded from further analysis. Weak hydrogen-bonding interactions of the type  $\text{C}-\text{H}\cdots\text{O}$  observed in some of the remaining structures do not destroy the above correlation.

A decrease in  $\text{C}''-\text{C}$  single-bond length and a simultaneous increase in  $\text{C}=\text{N}$  double-bond length in the nitron moiety are evidence of a conjugation in the enlarged bond system (Fig. 3*d*). By fitting the data to the modified Pauling's relationship (Pauling, 1960),  $10^{(\Delta d(\text{C}=\text{N})/c_{\text{C}=\text{N}})} + 10^{(\Delta d(\text{C}''-\text{C})/c_{\text{C}''-\text{C}})} = 3$ , *i.e.* assuming the sum of bond orders equals 3 for the neighbouring  $\text{C}''-\text{C}$  and  $\text{C}=\text{N}$  bonds, the constants  $c_{\text{C}''-\text{C}} = 0.401$  and  $c_{\text{C}=\text{N}} = 0.329$  were obtained. Values of the constants are small when compared with the typically quoted 0.71 for the bond length-bond order dependence for C atoms, and can be explained by the presence of electronegative oxygen and an additional unsaturated bond connected to the  $\text{C}''-\text{C}=\text{N}$  group.

The maximal lengthening of the  $\text{C}=\text{N}$  bond is observed for the specific benzochinone-like systems (Fig. 3*a* and Table 5: all cases with  $\text{X} = \text{C}sp^2$ ). The minimal bond length appearing in structures with a large deviation from planarity ( $\tau$  close to  $90^\circ$ ) should be

Table 5. Selected geometrical parameters of the  $C''-C=N(\rightarrow O)-C'$  moiety for 35 nitrone molecules

Refcode	N—O (Å)	C=N (Å)	N—C' (Å)	C''—C (Å)	C''=X (Å)	O—N=C (°)	C=N—C' (°)	O—N—C' (°)	$\tau^*$ (°)	$\varphi$ (°)
Nitrones with aromatic ring at C										
AMCBAO	1.298	1.299	1.464	1.472	†	124.6	120.3	115.0	55.0	—
CASTEV	1.286	1.309	1.461	1.455	†	123.5	123.3	113.2	14.0	85.8
CIPWED	1.308†	1.286	1.438	1.441	†	123.8	120.3	116.6	10.0	33.9
DAPXOH	1.276	1.302	1.526	1.448	†	122.8	123.7	113.3	17.2	—
DEDWEO	1.285	1.311	1.456	1.468	†	123.4	122.2	114.4	3.1	87.9
FAHYUI	1.315	1.303	1.469	1.476	†	120.8	124.0	115.2	69.8	—
FAHYUI	1.313	1.305	1.469	1.479	†	120.3	124.4	115.2	65.2	—
FEXBOZ	1.307	1.330	1.519	1.442	†	123.7	121.2	115.1	13.0	—
JIBFAB	1.293	1.324	1.453	1.474	†	125.0	122.2	112.7	44.6	67.2
KAMJAJ	1.300	1.308	1.480	1.477	†	122.0	123.1	114.8	56.7	—
KESNEB	1.274	1.306	1.524	1.444	†	123.0	122.2	114.7	8.1	—
MCBZOX	1.283	1.309	1.499	1.464	†	125.2	118.8	116.0	6.1	—
TAFRUN	1.322†	1.288	1.511	1.455	†	122.6	123.7	113.6	25.2	—
TPNITR	1.299	1.326	1.458	1.476	†	125.1	122.4	112.5	45.2	68.6
TPNITR01	1.305	1.310	1.449	1.474	†	125.1	123.1	111.8	44.5	68.6
VAXFUV	1.330†	1.297	1.524	1.469	†	125.5	122.6	111.8	17.5	—
Nitrones with $X = Csp^2$										
GASGAI	1.283	1.345	1.447	1.444	1.344	120.8	125.6	113.6	0.4	59.3
MXIDPO	1.266	1.357	1.448	1.437	1.357	122.6	121.3	116.1	2.5	59.5
VIVVOL	1.280	1.358	1.520	1.422	1.349	118.6	126.0	115.3	0.6	—
VIVVOL	1.277	1.367	1.529	1.421	1.358	119.3	124.0	115.9	0.4	—
Nitrones with $X = Nsp^2$										
N11	1.295	1.300	1.451	1.479	1.281	121.4	122.3	116.3	−123.5	24.8
N15	1.290	1.301	1.458	1.461	1.289	122.6	121.8	115.6	141.4	22.0
N22	1.290	1.312	1.458	1.470	1.293	124.2	119.6	116.2	−145.8	36.8
N25	1.289	1.310	1.453	1.467	1.294	123.2	120.9	115.9	144.8	29.0
N65	1.292	1.312	1.461	1.465	1.293	123.2	120.5	116.2	−145.8	29.4
Nitrones with $X = Osp^2$										
BOWZES	1.274	1.300	1.496	1.466	1.200	126.2	118.3	115.5	6.1	—
CEJVUI	1.274	1.295	1.511	1.469	1.183	125.9	118.1	115.8	−28.6	—
ETCBPO	1.279	1.284	1.571	1.538	1.264	124.1	123.2	112.6	74.3	—
KUJBEW	1.330†	1.311	1.451	1.488	1.194	118.4	127.4	114.2	12.3	—
KUJBEW	1.328†	1.311	1.469	1.485	1.201	118.4	126.0	115.3	22.9	—
Nitrones with $X = Csp^3$										
CINZII	1.299†	1.270	1.458	1.477	—	124.3	121.3	114.5	—	—
DIYRIM	1.308	1.287	1.490	1.443	—	124.5	119.9	115.6	—	—
SADHOU	1.304	1.290	1.545	1.525	—	120.0	124.8	115.1	—	—
SADHOU	1.305†	1.301	1.524	1.529	—	119.8	126.8	113.3	—	—
VIRJIP	1.290	1.291	1.478	1.480	—	124.6	120.6	114.8	—	—
Overall average	1.296	1.309	1.483	1.464	—	122.8	122.5	114.7	—	—
Standard error	0.003	0.004	0.006	0.004	—	0.4	0.4	0.2	—	—

\*  $\tau$  angle is taken as an average of two possible torsion angles in the cases where X belongs to aromatic or benzochinone-like systems.

† Aromatic bond.

‡ N→O involved in strong hydrogen bonding.

compared with the mean value calculated for unconjugated nitrones [1.289 (2) Å; Table 5,  $X = Csp^3$ ].

The relationship between the N—O bond length and  $\tau$  (Fig. 3c) is another interesting feature of the enlarged nitrone system. The lengthening of the N—O bond can be attributed to a decrease in  $\pi$ -conjugation in the enlarged conjugated nitrone system. The extreme N—O bond lengths given by linear regression are 1.278 (3) Å for  $\tau = 0^\circ$  (maximal conjugation, planar system) and 1.310 (3) Å for  $\tau = 90^\circ$  (conjugation excluded). The latter value was found to be in agreement with the mean bond length 1.301 (8) Å calculated for the molecules without double or aromatic bonds at  $C''$ .

Detailed inspection of Figs. 3(a)–(c) and Table 5 reveals a slightly different bond length distribution over the investigated  $X=C''-C=N\rightarrow O$  fragment, depend-

ing on the nature of X, i.e. O, N, C(ar) or  $Csp^2$ , respectively. Although the sample size in each case is too small to draw definite conclusions, it should be pointed out that the O atom in position X ( $C''=O$  group) has a competitive behaviour to that of the nitrone group ( $N\rightarrow O$ ). Here the conjugation is observed in the  $C''-C=N\rightarrow O$  region with the N—O bond length [1.278 (3) Å] significantly shortened in relation to the unconjugated nitrones [1.301 (8) Å], whereas the  $C''=O$  bond length remains short and almost unaffected. For X substituted by N or C(ar), the conjugation is equally extended in the whole chain of  $X=C''-C=N\rightarrow O$  with the N—O bond length intermediate between 1.301 (8) and 1.276 (2) Å. In the case of benzochinones ( $X = Csp^2$ , full conjugation:  $\tau \approx 0^\circ$ ), the N—O bond length 1.277 (2) Å is shortened in a similar way as for  $X = O$ ,

however, its change is not related to the  $\tau$  angle chosen as a measure of the degree of conjugation.

Contrary to the conclusions of Arumugam, Manisankar, Sivasubramanian & Wilson (1984) and Moskal & Milart (1985), the phenyl ring at the nitrone N atom (ring C) is not coplanar with the  $X=C''-C=N\rightarrow O$  system and additionally there was no correlation found between the  $\varphi$ -angle [ $\varphi = C-N-C''(\text{ar})-C(\text{ar})$ ] and any of the geometric parameters of the nitrone system for structures with the C' atom in a phenyl ring.

All statistical calculations were performed using *STATGRAPHICS PLUS* (Statistical Graphics Corporation, 1992).

### Concluding remarks

The enlargement of the nitrone moiety by a double or aromatic bond has a significant influence on  $C=N\rightarrow O$  geometry due to  $\pi$ -electron conjugation. The conjugation is controlled by the torsion angle  $X=C''-C=N$ . Shortening of the N—O bond length of the conjugated nitrones [up to 1.278 (3) Å for  $\tau = 0^\circ$ ] in relation to 1.301 (8) Å, which is specific for unconjugated nitrones, was found to be determined both by a degree of the conjugation in the enlarged system and by the competitive influence of the electronegative nature of the X substituent. The possible elongation of the N—O bond

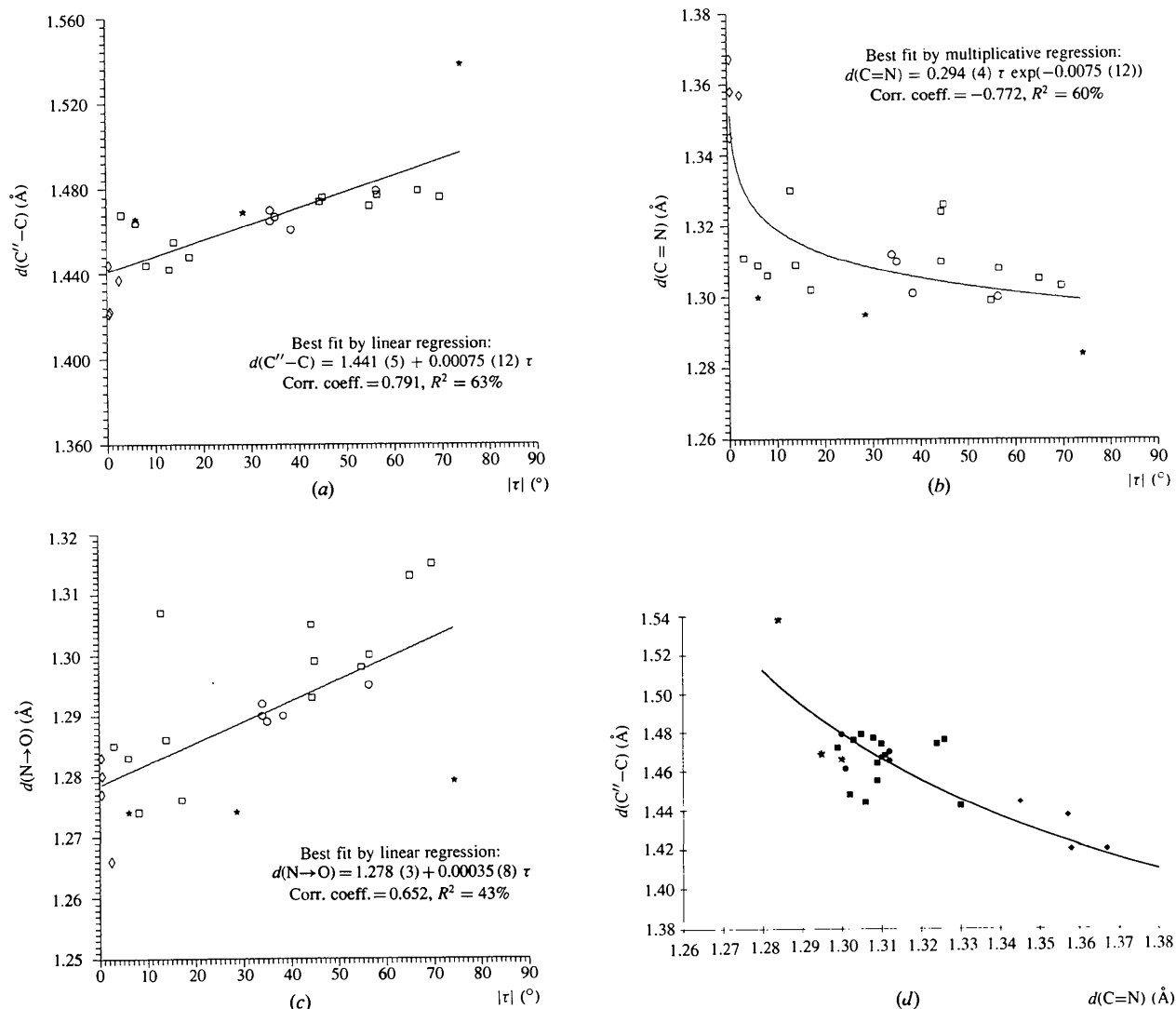


Fig. 3. Bond lengths (a)  $C''-C$ , (b)  $C=N$  and (c)  $N\rightarrow O$  as a function of  $|\tau|$  angle for a sample of 25 nitrones. Molecules with  $X = C(\text{ar})$  are marked as squares,  $X = Csp^2$  as diamonds,  $X = N$  as circles and  $X = O$  as asterisks. For anticlinal conformation  $\tau$  is taken as  $180^\circ - |\tau|$ . The molecules forming strong  $N\rightarrow O \cdots H-O$  hydrogen bonds are omitted. (d) Scatterplot of  $C''-C$  versus  $C=N$  bond length and fitted curve corresponding to Pauling's relationship with minimized values of parameters  $c_{C''-C} = 0.401$  and  $c_{C=N} = 0.329$ ; strong negative correlation (correlation coefficient = -0.750) is found.

length was observed only for nitron oxygen being involved in strong hydrogen bonding. The presented nitron, as well as all other conjugated nitrones of 1,4-diazabutadiene systems, fulfil to a high extent all discovered relationships.

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## High-Pressure X-ray Diffraction Study of Pentaerythritol

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### Abstract

Pentaerythritol [2,2-bis(hydroxymethyl)-1,3-propanediol],  $C(CH_2OH)_4$ , tetragonal,  $I\bar{4}$ ,  $Z = 2$ ,  $a = 6.0752$  (8),  $c = 8.733$  (2) Å at  $T = 291$  K and 0.1 MPa, has been studied at high pressures by X-ray diffraction. The pressure dependence of the unit-cell dimensions has been measured to 1.15 GPa, and the crystal structure has been

determined at 1.15 GPa:  $a = 6.017$  (1),  $c = 8.267$  (3) Å; final  $R = 0.043$  for 185 observed reflections; the C and O atoms were refined with anisotropic thermal parameters, and H atoms located in a  $\Delta F$  map and refined with isotropic thermal parameters. The compressibility of van der Waals contacts between the sheets of the hydrogen-bonded molecules is several times larger than along the sheets, and above 280 MPa the distances between the