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2,2′-Diphenyl-$\Delta^{3,3'}$-bi-3*H*-indole-1,1′-dioxide: Molecular Interactions and Crystal Structure

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The Dinitrone 2,2′-diphenyl-$\Delta^{3,3'}$-bi-3*H*-indole-1,1′-dioxide acts as a demethylating and dehydrogenating agent. The mechanism of interaction of the dinitrone with donors and acceptors does not involve intermediate charge-transfer complexes probably due to a self association between dinitrone molecules (as supported by X-ray determinations). The crystal structure of the dinitrone was obtained by direct methods; $a = 9.967(2)$, $b = 19.817(3)$, $c = 10.875(2)$ Å, $\beta = 111.2(2)°$, space group $P2_1/n$. The final R and R_w were 0.089 and 0.063 for all measured reflexes.

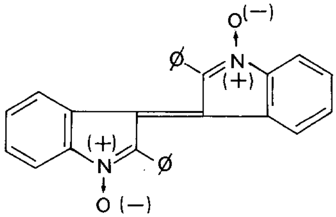
(Keywords: Charge transfer complexes; Molecular associations; 2,2′-Diphenyl-$\Delta^{3,3'}$-bi-3H-indole-1,1′-dioxide)

2,2′-Diphenyl-$\Delta^{3,3'}$-bi-3H-indol-1,1′-dioxid: Molekulare Wechselwirkungen und Kristallstruktur

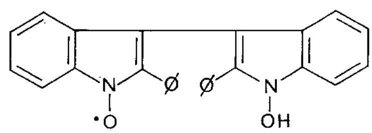
Das Dinitron 2,2′-Diphenyl-$\Delta^{3,3'}$-bi-3*H*-indol-1,1′-dioxid wirkt als Demethylierungs- und Oxydationsmittel. Die Wechselwirkung des Dinitrons mit Elektronen-Acceptoren und Elektronen-Donatoren geht wegen der Selbstassoziation zwischen den Dinitron-Molekülen ohne die dazwischenliegende Bildung eines Charge-Transfer-Komplexes vor sich; das wird auch von Röntgenstrukturuntersuchungen gestützt. Die Kristallstruktur wurde mit direkten Methoden ermittelt: $a = 9.967(2)$, $b = 19.817(3)$, $c = 10.875(2)$ Å; $\beta = 111.2(2)°$. $P2_1/n$. Die endgültigen Werte R und R_w waren 0.089 und 0.063 für alle gemessenen Reflexe.

Introduction

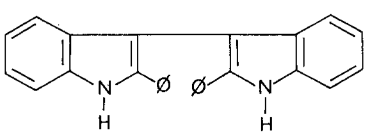
For a long period of time the dinitrone 2,2′-diphenyl-$\Delta^{3,3'}$-bi-3*H*-indole-1,1′-dioxide (**I**) has been used as oxidizing agent toward various electron donating compounds [1]; in addition, compound **I** induces interesting demethylation reactions on aromatic hydrocarbons and on several nitrogen bearing compounds (pyridines, amides, amines) [2, 3]. The formation of molecular association between the dinitrone **I** and donor compounds was assumed in the course of the cited reactions. On the other hand, it also exhibits radical character due to the presence of small amounts (0.5%) of mononitroxide radical **I′**. Some precursors to **I** (1-hydroxy-2-phenylindole and compounds **II** and **III**), act as good donors in molecular complexes formation [4–6].



I



I'



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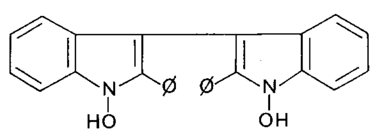
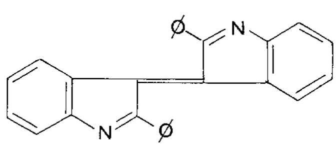


III



IV

Attempts to use the compound **I** for the formation of charge-transfer complexes (CTC) was unsuccesful: classical donors (e.g., N,N-dimethylaniline) or acceptors (e.g., tetracyanoethylene, *TCNE*) were not able to form (in dichloroethane solution) any molecular association with **I**, as evidenced by electronic (UV-vis) and infrared spectra.

Recent literature reports [7] describe the formation of CTC between heterocyclic nitrones and classical acceptors (*TCNE*, 1,4-benzoquinones). In order to better understand all the above results a X-ray investigation on the molecule of the dinitrone **I** was undertaken.

Results and Discussion

Table 1 reports the final atomic coordinates of the molecule. The bond distances and angles of the molecule, shown on (001) in Fig. 1, are given in Table 2. Least-squares calculations show that the individual parts of the molecule are planar and that the maximum deviation from planarity is at C 15 and C 18 of one of the five-membered rings (out-of-plane = 0.022 Å). The two fused rings of the indole moieties are bent by 5.9 (1) and 1.6 (1)° to each other in the two half-molecules, respectively. The two oxygen atoms are out of the C—N—C planes by 0.016 (3) and 0.292 (3) Å and by 0.028 (3) and 0.076 (3) Å from the best planes through the five-membered rings. These values correspond to angles of 1.1 (2) and 3.5 (2)° between the N—O bonds and the five-membered planes and are comparable with that of 2° observed in 3-acetyl-1-methoxyindole [8] and 3.8° in (*R*)-(+)-3-carboxy-2,2,5,5-tetramethylpyrrolidine-1-oxyl [9]. A degree of pyramidality at N2 (which is out by 0.033 Å with respect to the plane of the three connected atoms) is noticeable when compared with N1 [deviation 0.006 (3) Å].

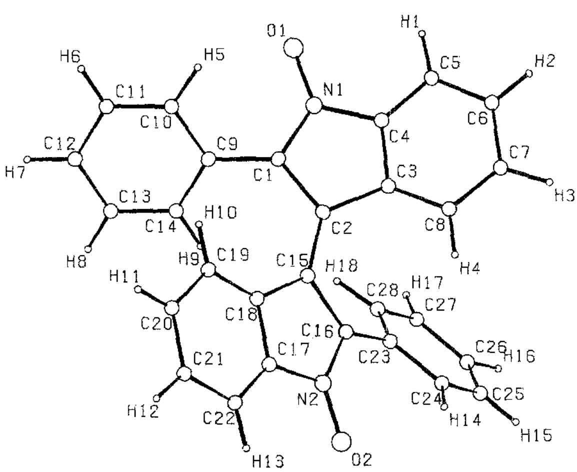


Fig. 1. Projection of the structure of 2,2′-Diphenyl-$\Delta^{3,3'}$-bi-3H-indole-1,1′-dioxide (**I**) along 001

Table 1. *Atomic fractional coordinates* (× 10^4) *and U*-EQ (× 10^4 Å^2) *of dinitrone* **I**

	X/A	Y/B	Z/C	U-EQ
O1	4187(2)	3431(1)	1353(2)	819(9)
O2	5367(2)	-651(1)	3071(2)	731(9)
N1	4662(3)	2840(1)	1762(2)	642(9)
N2	4938(2)	-40(1)	2995(2)	586(8)
C1	3884(3)	2281(1)	1778(3)	587(11)
C2	4885(3)	1734(1)	2292(3)	551(10)
C3	6331(3)	2015(1)	2592(3)	582(11)
C4	6156(3)	2695(1)	2259(3)	622(12)
C5	7273(4)	3141(1)	2472(3)	738(16)
C6	8642(4)	2894(1)	3087(3)	776(17)
C7	8863(3)	2226(1)	3484(3)	739(13)
C8	7711(3)	1783(1)	3242(3)	656(13)
C9	2327(3)	2272(1)	1169(3)	594(11)
C10	1485(3)	2811(1)	1307(3)	657(12)
C11	24(4)	2799(1)	723(3)	748(15)
C12	-665(4)	2251(2)	-27(3)	773(14)
C13	150(3)	1714(1)	-193(3)	715(13)
C14	1622(3)	1727(1)	389(3)	627(12)
C15	4570(2)	1072(1)	2558(2)	545(10)
C16	5425(3)	494(1)	2511(2)	552(10)
C17	3737(3)	149(1)	3342(2)	569(9)
C18	3453(3)	832(1)	3038(2)	556(10)
C19	2358(3)	1123(1)	3353(3)	640(11)
C20	1555(3)	722(1)	3881(3)	714(13)
C21	1852(3)	42(1)	4131(3)	707(12)
C22	2988(3)	-257(1)	3891(3)	657(12)
C23	6417(3)	405(1)	1817(2)	551(10)
C24	7599(3)	-23(1)	2267(3)	659(12)
C25	8462(3)	-124(1)	1540(3)	739(13)
C26	8157(3)	202(1)	337(3)	754(14)
C27	7009(3)	635(1)	-107(3)	689(13)
C28	6132(3)	736(1)	604(3)	613(11)

The geometrical values in the rings suggest a certain delocalisation of the N—O and N—C bonds in the direction of the aromatic rings. In fact the N—O distances are intermediate between double (1.20 Å) and single (1.44 Å) bonds; the N1—C1 and N2—C16 bonds are shorter than those N1—C4 and N2—C17, and, finally, the C1—C9 and C2—C15 bonds are both significantly shorter than the accepted C_{sp^2}—C_{sp^2} single bond value (1.482 Å [10]).

The molecules are held in the crystal by *Van der Waals* forces and a view of the packing is represented in Fig. 2.

π-π interactions are responsible for the formation of molecular complexes, in solution, between indoles and *TCNE* [11, 12], while a strong hydrogen bond is responsible for the formation of complexes: (i) between the N—OH bond of 1-hydroxy-2-phenylindole and azylazopyridines [4], (ii) between the N—OH bond of 2,2′-diphenyl-$\Delta^{3,3'}$-bi-3*H*-indole-1,1′-dihydroxide and arylazopyridines (or the corresponding N-oxides) [2]. On the other hand, the N—O bond of aromatic and aliphatic

Table 2. *Bond distances* (Å) *and angles* (°) *of dinitrone* **I** *with estimated deviations in parentheses*

O1-N1	1.281(3)	C11-C12	1.382(5)
O2-N2	1.277(3)	C12-C13	1.390(5)
N1-C1	1.356(4)	C13-C14	1.372(4)
N1-C4	1.418(4)	C15-C16	1.440(3)
N2-C16	1.348(3)	C15-C18	1.469(4)
N2-C17	1.429(4)	C16-C23	1.455(5)
C1-C2	1.442(3)	C17-C18	1.398(3)
C1-C9	1.451(5)	C17-C22	1.372(4)
C2-C3	1.468(4)	C18-C19	1.383(5)
C2-C15	1.403(3)	C19-C20	1.391(5)
C3-C4	1.390(3)	C20-C21	1.385(3)
C3-C8	1.378(4)	C21-C22	1.384(5)
C4-C5	1.374(4)	C23-C24	1.389(4)
C5-C6	1.374(5)	C23-C28	1.407(4)
C6-C7	1.385(3)	C24-C25	1.377(5)
C7-C8	1.393(4)	C25-C26	1.391(4)
C9-C10	1.400(4)	C26-C27	1.371(4)
C9-C14	1.396(4)	C27-C28	1.375(5)
C10-C11	1.362(5)		

O1-N1-C4	121.5(3)	C4-C5-C6	117.0(2)	N2-C17-C22	126.9(2)
O1-N1-C1	127.6(4)	C5-C6-C7	120.7(4)	N2-C17-C18	108.0(3)
C1-N1-C4	110.9(2)	C6-C7-C8	121.1(3)	C18-C17-C22	125.1(3)
O2-N2-C17	121.6(3)	C3-C8-C7	119.2(2)	C15-C18-C17	106.4(4)
O2-N2-C16	127.6(3)	C1-C9-C14	120.5(3)	C17-C18-C19	117.1(3)
C16-N2-C17	110.6(2)	C1-C9-C10	121.7(3)	C15-C18-C19	136.1(2)
N1-C1-C9	121.8(2)	C10-C9-C14	117.8(4)	C18-C19-C20	119.2(2)
N1-C1-C2	107.5(3)	C9-C10-C11	121.2(2)	C19-C20-C21	121.5(4)
C2-C1-C9	130.1(2)	C10-C11-C12	120.5(3)	C20-C21-C22	120.7(3)
C1-C2-C15	127.4(4)	C11-C12-C13	119.3(4)	C17-C22-C21	116.2(2)
C1-C2-C3	106.7(2)	C12-C13-C14	120.2(3)	C16-C23-C28	119.0(3)
C3-C2-C15	125.7(4)	C9-C14-C13	120.9(2)	C16-C23-C24	122.7(3)
C2-C3-C8	134.8(2)	C2-C15-C18	129.1(3)	C24-C23-C28	118.2(4)
C2-C3-C4	106.8(4)	C2-C15-C16	123.9(3)	C23-C24-C25	120.8(3)
C4-C3-C8	117.7(3)	C16-C15-C18	106.8(2)	C24-C25-C26	120.2(3)
N1-C4-C3	108.1(4)	N2-C16-C15	109.0(3)	C25-C26-C27	119.5(4)
C3-C4-C5	124.2(3)	C15-C16-C23	129.6(2)	C26-C27-C28	120.8(3)
N1-C4-C5	127.5(2)	N2-C16-C23	121.0(2)	C23-C28-C27	120.4(3)

amine N-oxides is the active center for molecular complexes formation with acceptors like iodine [13] or *TCNE* (unpublished results).

Either electronic or steric factors may be responsible for the failure by dinitrone **I** to form CTC.

Two evidences may support the first hypothesis: (i) the extended conjugation between the indole moiety and the N—O bond (X-ray measurements show shorter bond lengths in N—O and N—C bonds) that may reduce the ability of N—O in CT bonding, (ii) the fact that 2,2′-diphenyl-3,3′-bis-indolenine, **IV** (which has almost the same aromatic electronic situation as dinitrone **I**) does not form intermediate CT bonding with *TCNE* and dimethyl aniline (unpublished results).

On the other hand, with acceptors characterized by a high electron affinity (Tetracyanoethylene, Fluoranil, 2,3-Dichloro-5,6-dicyano-1,4-

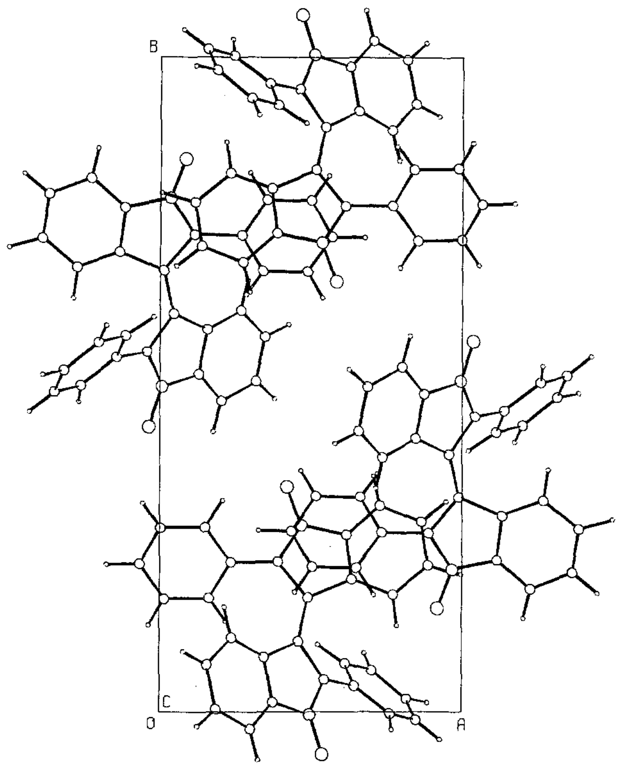


Fig. 2. Packing of compound **I** along 001

benzoquinone), the nitrones act as π base and form, in solution, stable 1 : 1 charge-transfer complexes [7].

X-ray reasurements show that the phenyl groups of dinitrone **I** are tilted by 39.6° with respect to the mean indole plane. Normally, 2-phenylindole molecules as a whole are characterized by a nearly planar conformation with the phenyl group lying at quite small angles with respect to the indole planes [4]. Furthermore the mean planes of the indole rings are tilted by about 40°, while the flap angles within the indole rings are 5.9° and 1.6°.

In addition to the above remarks one may suppose that dinitrone **I** exists as a self complex, according to the following evidences: (i) the intense colour of **I** in solution and in the solid state; (ii) the crystalline structure for example, see packing of molecules along the z axis in Fig. 2, where nitrone molecules are faced through the phenyl and indole moieties in ordered stacks, suggesting a π-π interaction (a similar situation can be found in some hydrocarbons [14], or in the crystalline structure of tricyanovynilidene-phenylhydrazones which surprisingly do not behave as amphoteric CTC partners as expected from studies on similar compounds [15]); (iii) the conductivity of dinitrone **I** that is noticeably higher (1.10^{-8} ohm^{-1} cm^{-1}) than those of biindole **II** (8.10^{-12} ohm^{-1} cm^{-1}) and of 1-hydroxy-2-phenylindole (5.10^{-11} ohm^{-1} cm^{-1}).

Usually, small differences in conductivity values may be evidenced among pyridines and the corresponding N-oxides.

Probably we are in the presence of a weakly bonded self complex as evidenced by the fact that the molecules of dinitrone **I** are held together by normal *Van der Waals* forces. With quinonoid acceptors, like 2,3,5,6-tetrachloro-1,4-benzoquinone (Chloranil) or 2,3-dicyano-5,6-dichloro-1,4-benzoquinone (*DDQ*), the dinitrone **I** did not show CT interactions either in the solid state or in solution.

Experimental

Compounds and Solvents

2,2'-diphenyl-$\Delta^{3,3'}$-bi-indole-1,1'-dioxide (**I**), 2,2'-diphenyl-$\Delta^{3,3'}$-bi-3H-indole (**II**) and 2,2'-diphenyl-$\Delta^{3,3'}$-bi-3H-indole-1,1'-dihydroxide (**III**) were obtained according to *Colonna* [16].

All other compounds and solvents were Fluka RP ACS grade reagents and purified before use.

Spectroscopy

UV-Vis, IR spectra were measured on Perkin-Elmer 554, 298 instruments, respectively.

X-ray Analysis of Compound **I**

Intensity data were collected at room temperature using the Ni-filtred CuKα radiation ($\lambda = 1.54178$ Å) on a Siemens AED single crystal diffractometer equipped with a Jumbo 220 General Automation computer. Alignement or decomposition of the crystal ($0.2 \times 0.3 \times 0.6$ mm) was controlled on one reflection monitored every fifty measurements. The profile analysis procedure [17] modified by *Belletti, Ugozzoli, Cantoni* and *Pasquinelli* [18] was employed. *Lorentz* and polarisation effects were corrected, absorption was ignored. The compound is monoclinic, space group $P2_1/n$, $a = 9.967(2)$, $b = 19.817(3)$, $c = 10.875(2)$ Å, $\beta = 111.1(2)°$, $V = 2002.6(8)$ Å^3, $M = 414.46$, $Z = 4$, $D_c = 1.37$ gcm^{-3}, $\mu = 6.56$ cm^{-1}. 4097 reflections were measured ($2 \leqslant \Theta \leqslant 70°$) (3760 independent) and 2207 were considered observed at 2 (I) level. The structure was solved by direct methods with SHELX [19] and refined by block-matrix least-squares anisotropically. The H atoms, found in a *Fourier* difference synthesis, were refined isotropically. 8 reflections were omitted in the last cycles because probably affected by extinction. The final agreement values were $R = 0.089$ and $R_w = 0.063$ with $w = 1.0/(^2F + 0.003\,F^2)$ for all the reflections, $S = 0.901$*. The final *Fourier*

* Lists of structure factors, H coordinates, bond distances involving H atoms and a table of least-squares calculations are available upon request from one of the authors (*G. B.*).

difference synthesis was without residual peaks > 0.24 eÅ^{-3}; $(\Delta/\sigma)_{max} = 0.619$ for heavy atoms; the scattering factors used throughout the analysis were those of SHELX. Atomic coordinates are in Table 2. All the calculations were performed on the CDC CYBER 76 computer of the CINECA (Casalecchio, Bologna).

Electrical Conductivities

Values of σ were determined at 25 °C and 1 min after voltage application, using a thermostated cell under a nitrogen stream. Applied field 10 000 Vcm^{-1}. The pellets of samples, obtained under pressure, had a diameter of 5 mm.

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