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## A Nitroxide Tetradical Exhibiting Ferromagnetic Coupling

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### Abstract

The crystal structure of a nitroxide radical exhibiting ferromagnetic exchange interactions is described. The closest NO· · · NO contact in 4,4',4''4'''-[1,2,4,5-benzene-tetrayltetrakis(carbonyloxy)]tetrakis(2,2,6,6-tetramethyl-1-piperidinyloxy), C<sub>46</sub>H<sub>70</sub>N<sub>4</sub>O<sub>12</sub>, involves an orthogonal arrangement of two nitroxide groups, leading to a ferromagnetic exchange interaction.

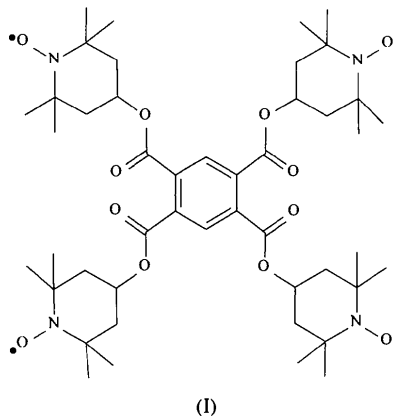
### Comment

The synthesis and characterization of new organic compounds showing cooperative magnetic phenomena is currently an area of increasing interest. However, a well characterized chemically stable organic ferromagnet which has an ordering temperature about room temperature is not yet available. A necessary condition for the existence of such a 'molecular ferromagnet' consisting of molecular units is the occurrence of an inter- or intramolecular ferromagnetic exchange interaction.

Very few metal-free organic radicals have been reported to exhibit magnetic ordering. The series of nitroxides provides probably the most efficient source of organic compounds exhibiting extended magnetic interactions (Rassat, 1990). Many of them form linear chains, with some showing three-dimensional magnetic ordering at very low temperatures. However, only a limited number of these nitroxide radicals possess positive Weiss constants and the mechanism which may provide such ferromagnetic exchange interactions is not

yet completely explained. For compounds containing 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) radical groups, the occurrence of a positive Weiss constant was explained in terms of the assumption of dipolar interactions between the adjacent spin centres (see for example Miller & Epstein, 1994). However, the structural arrangement which may provide this spin pairing is still under discussion.

This has prompted us to resynthesize a nitroxide tetradical and investigate the magnetic properties on the basis of X-ray structure investigations. The synthesis and some EPR data of this compound, (I), have been reported previously by Sholle, Prokop'ev, Sortova, Sarymsakov & Rozantev (1981). The effective magnetic moment increases gradually with decreasing temperature. This clearly indicates the existence of a ferromagnetic exchange interaction which can be described by a Curie–Weiss law with a positive Weiss constant of +0.7 (1) K.



The crystal structure of (I) has two centrosymmetric molecules in the unit cell, the asymmetric unit being half a molecule (Fig. 1). The intramolecular bond distances and angles within the TEMPO rings have expected values, such as those observed by Seff (1972). Of particular importance with respect to the dipolar interaction between the spin centres is the distance between the nitroxide NO groups and their relative orientation. The closest contacts between nitroxide O atoms are 4.184 (3) [O1· · · O1(2 - x, y - 1/2, 3/2 - z), intermolecular] and 4.974 (3) Å [O6· · · O1(1 - x, y - 1/2, 3/2 - z), intermolecular]. The O1· · · N1(2 - x, y + 1/2, 3/2 - z) distance is 3.545 (3) Å. The N· · · O bonds corresponding to the closest O(nitroxide) contacts are approximately perpendicularly oriented [angles O1· · · N1<sup>i</sup>—O1<sup>i</sup> 111.4(1) and N1—O1· · · N1<sup>i</sup> 168.8(1)°; symmetry code: (i) 2 - x, y + 1/2, 3/2 - z]. The near orthogonality is not a consequence of symmetry. This arrangement, leading to orthogonal magnetic orbitals, is most probably the origin of the ferromagnetic interactions in the title compound.

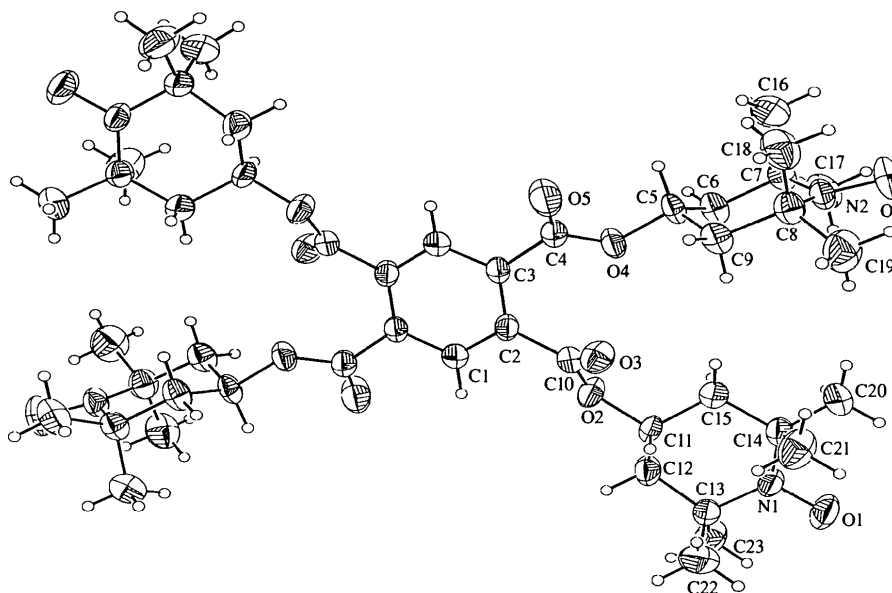


Fig. 1. The molecular structure of (I) with the atom labelling and 50% probability displacement ellipsoids.

## Experimental

The synthesis of the tetradical was carried out following essentially the synthetic route described by Falle *et al.* (1966) for similar paramagnetic esters of benzene- or biphenylpolycarboxylic acid. Orange-red crystals of the title compound were recrystallized from ethanol. The magnetic susceptibility measurement in the temperature range 4.2–300.0 K was carried out using a Faraday system.

### Crystal data

$C_{46}H_{70}N_4O_{12}$   
 $M_r = 871.06$   
 Monoclinic  
 $P2_1/c$   
 $a = 11.799$  (2) Å  
 $b = 8.155$  (2) Å  
 $c = 25.063$  (3) Å  
 $\beta = 91.11$  (1)°  
 $V = 2411.1$  (8) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 1.200$  Mg m<sup>-3</sup>  
 $D_m$  not measured

### Data collection

Enraf-Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: empirical  $\psi$  scan (North, Phillips & Mathews, 1968)  
 $T_{\min} = 0.901$ ,  $T_{\max} = 0.999$   
 5683 measured reflections  
 3330 independent reflections

Mo  $K\alpha$  radiation  
 $\lambda = 0.71069$  Å  
 Cell parameters from 25 reflections  
 $\theta = 3.25$ – $13.60$ °  
 $\mu = 0.086$  mm<sup>-1</sup>  
 $T = 297$  (2) K  
 Needle  
 $0.50 \times 0.20 \times 0.13$  mm  
 Orange

2392 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.022$   
 $\theta_{\text{max}} = 22.98$ °  
 $h = -12 \rightarrow 7$   
 $k = 0 \rightarrow 8$   
 $l = -27 \rightarrow 27$   
 3 standard reflections  
 frequency: 120 min  
 intensity decay: 1.4%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.127$   
 $S = 0.861$   
 3328 reflections  
 280 parameters  
 H atoms riding  
 $w = 1/[\sigma^2(F_o^2) + (0.0918P)^2 + 0.8293P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.005$   
 $\Delta\rho_{\text{max}} = 0.221$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.157$  e Å<sup>-3</sup>  
 Extinction correction: none  
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °) and contact distances (Å)

N1—O1	1.279 (2)	O1···O1 <sup>iii</sup>	4.184 (1)
N2—O6	1.282 (2)	O6···O1 <sup>iii</sup>	4.974 (1)
O1···N1 <sup>i</sup>	3.545 (3)		
O1—N1 <sup>i</sup> —O1 <sup>i</sup>	111.4 (1)	N1—O1—N1 <sup>i</sup>	168.8 (1)

Symmetry codes: (i)  $2 - x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (ii)  $2 - x, y - \frac{1}{2}, \frac{3}{2} - z$ ; (iii)  $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$ .

Data collection: *SDP* (Frenz, 1985). Cell refinement: *SDP*. Data reduction: *REDU4* (Stoe & Cie, 1991). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PLUTON93* (Spek, 1993). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1074). Services for accessing these data are described at the back of the journal.

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### Unique *trans-syn-cis* [6.6.7] Tricycle Derivative from Transannular Diels–Alder Contraction of a Model 15-Membered *trans-cis-cis* Macrocylic Triene

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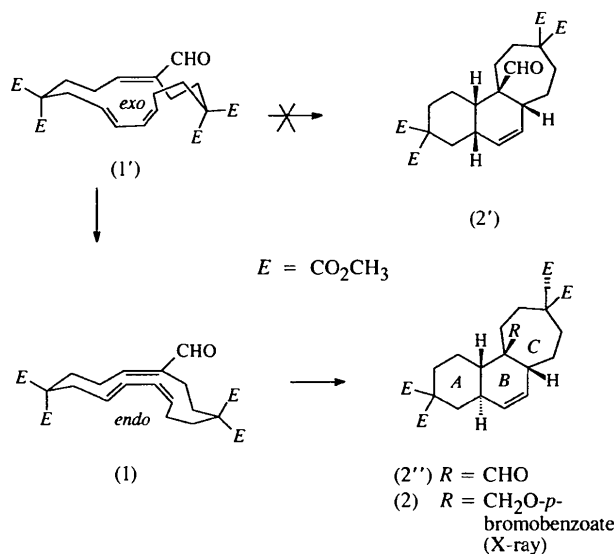
#### Abstract

A model 15-membered *trans-cis-cis* macrocylic triene, (*trans-cis-cis*)-tetramethyl (4*E*,11*Z*,13*E*)-5-formylcyclopentadeca-4,11,13-triene-1,1,8,8-tetracarboxylate, C<sub>24</sub>H<sub>32</sub>O<sub>9</sub>, was synthesized and led to the exclusive formation of a *trans-syn-cis* [6.6.7] tricyclic compound upon a transannular Diels–Alder reaction. The structure of the precursor and a *p*-bromobenzoyl analog of the product, (*trans-syn-cis*)-tetramethyl *rac*-(1*S*,2*S*,7*R*,10*R*)-(8*Z*)-1-(4-bromobenzoyloxymethyl)tricyclo[8.5.0.0<sup>2,7</sup>]pentadec-8-ene-5,5,13,13-tetracarboxylate ethanol solvate, 3C<sub>31</sub>H<sub>37</sub>BrO<sub>10</sub>·0.76C<sub>2</sub>H<sub>6</sub>O, were determined in order to establish their exact geometries and ring-junction stereochemistries.

#### Comment

The power of the transannular Diels–Alder (TADA) reaction of 15-membered macrocylic trienes for the

stereoselective generation of an *ABC* [6.6.7] tricyclic steroid skeleton in a single chemical step has recently been demonstrated (Hall, Müller & Deslongchamps, 1995*a,b*). We reported thereafter the crystal structure of such a condensed ring structure with *trans-anti-cis* (TAC) ring-junction stereochemistry (Michel, Drouin & Hall, 1995). This structure was the result of a facile cycloaddition on a *trans-trans-trans*-cyclopentadecatriene. We now report the crystal structure of a novel *trans-syn-cis* (TSC) *ABC* [6.6.7] tricyclic, (2), related to the important bioactive natural products aphidicolin (Dalziel, Hesp, Stevenson & Jarvis, 1973) and the scopadulan family (Hayashi *et al.*, 1987).



The tricyclic adduct (2) derives from a stereospecific Lewis acid-catalyzed TADA reaction of the formyl-substituted *trans-cis-cis* (TCC) cyclopentadecatriene (1) (Hall *et al.*, 1995). In order for (1) to collapse into compound (2'), the *trans-cis* diene moiety of (1) would have to adopt the unfavorable *cisoid* form characterized by strong allylic interactions of the internal methylene (1'). In such a form, the macrocycle may react through an *exo* approach leading to a highly strained transition-state structure having a *trans*-diaxial ring junction between incipient ring *B* in a boat conformation and the seven-membered ring *C*. Consequently, the corresponding *cis-syn-trans* tricyclic adduct (2') is not actually observed. Alternatively, the *endo* approach is freed of any particular ring strain or non-bonded interactions. Hence, after the TADA reaction, the corresponding TSC tricyclic (2'') is obtained exclusively. Its *p*-bromobenzoyl derivative, (2), as well as the parent cyclopentadecatriene, (1), could be crystallized and the ensuing X-ray diffraction analysis established their structures.

*ORTEP* (Johnson, 1995) perspective views of the macrocycle (1) and the tricyclic adduct (2) (three in-