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Nitration of 2,7-Di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene. Electrochemical Inquiry into Interaction Between Substituents in a Hückel 4n+2 System

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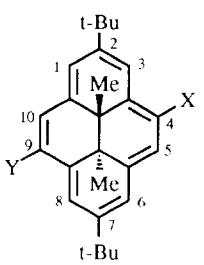
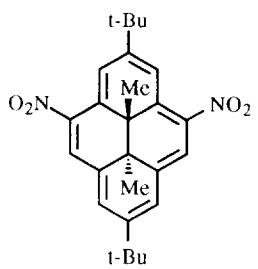
Key words: Electrochemistry; Non-benzenoid; Nitro compounds; Nitration; X-ray crystallography

Abstract: *A revised structure is reported for the product of dinitration of 2,7-di-t-butyl-10b,10c-dimethyl-10b,10c-dihydropyrene. The novel ortho-dinitro orientation and the electrochemical behavior of the mono and dinitro compounds are compared with the corresponding benzenoid substances.*

Relatively few studies have addressed the ways in which the physical and chemical properties of Hückel *4n+2* nonbenzenoid hydrocarbons[1] compare with those of related benzenoid substances. We report results bearing on this point. Nitration of 2,7-di-t-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (**1a**) was reported earlier to afford the 4,9-dinitro derivative (**1c**).[2] Structure **1c** was assigned because in



1a, X = Y = H
b, X = NO_2, Y = H
c, X = Y = NO_2



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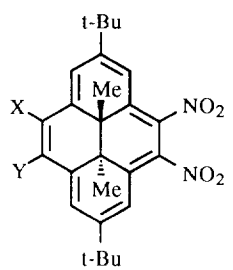


3a, X = Y = H
b, X = H, Y = NO_2
c, X = Y = NO_2

the ^1H NMR spectrum of the substance the methyl and *tert*-butyl groups appear as singlets at δ −2.93 (6 H) and 1.64 18H), respectively, and the ring protons are singlets at δ 8.41 (2 H), 8.42 (2 H) and 8.91 (2H), implying that the methyl and *tert*-butyl groups are in identical environments. The spectrum was therefore considered more consistent with structure **1c** than with the unsymmetrical structure **2**. *Ortho*-structure **3a** was not considered

because the nitro group is not an *ortho*-director. However, this structural assignment was not definitive, inasmuch as model compounds for these substances were not available at that time. It could have been argued that the nitro groups are too far from the alkyl groups to exert a meaningful effect. The present study was undertaken to clear up this ambiguity and to examine the effects of nitro groups on the electrochemical behavior of the conjugated ring system. The electrochemical behavior of this dihydropyrene ring system is relatively well-understood[3] and is consistent with the behavior of many other non-benzenoid aromatic hydrocarbons.[1b] Yet, almost no studies have compared the electrochemical behavior of *substituted* non-benzenoid aromatic[4] substances with their benzenoid counterparts. The availability of the putative **1c** presented an opportunity to examine this question. We report herein further structural studies, which have led to a revised structure for this substance, as well as electrochemical and computational studies on it and the dianion produced by its reduction.

RESULTS

Synthesis of Nitro Compounds. We have now synthesized the mononitro compound **1b** in 75% yield by nitration of **1a** with an equimolar amount of cupric nitrate trihydrate along with recovery of some **1a** (Table 1). The ^{1}H NMR spectrum of **1b** ($CDCl_3$) consists of singlets at δ -3.75 (3H), -3.74 (3H), 1.68 (9H), and 1.72 (9H) and resonances at δ 8.51 (1H, d, J = 8 Hz), 8.60 (1H, d, J = 8 Hz), 8.61 (1H, d, J = 1 Hz), 8.62 (1H, s), 8.69 (1H, s), 9.19 (1H, s), and 9.71 (1H, d, J = 1 Hz). The most striking features of the spectrum are the unusually low field resonances at δ 9.71 and 9.19, which are clearly associated with the protons at C-3 and C-5, respectively. The very large downfield shift of H–3 is presumably a result of the combined inductive, resonance, and anisotropic effects of the nitro group. Referring again to structures **1c** and **2**, each would be expected to exhibit two such low field two-proton resonances near δ 9.2 and 9.7 and therefore both must be rejected. Structure **2** can also be excluded by the fact that the nonequivalent methyl and *tert*-butyl groups in **1b** give rise to detectably different resonances as a result of the effect of the nitro group; this effect would be even more pronounced in **2**. Since nitration is unlikely to take place *ortho* to the bulky t-butyl groups,[5] the most likely structure for the dinitro compound appeared at this point to be the 4,5-dinitro, or *ortho*, derivative **3a**. The absence of a low-field resonance at *ca.* δ 9.7 can be explained by the reasonable assumption that the nitro groups in **3a** are twisted out of planarity because of steric interactions with each other.[6] The structure of **3a** has now been confirmed definitively by X-ray crystallographic analysis. The structure (Fig. 1) in fact clearly shows the two *ortho*-nitro groups twisted out of planarity (16.1 degrees), as implied by the ^{1}H NMR spectrum. The 4,5,9-trinitro compound **3b** can be obtained by nitration of **1a** with 3.1 equiv. of cupric nitrate trihydrate under the same reaction conditions and it does indeed exhibit a low-field resonance at δ 9.43 for H_8. Nitration of **1a** with 4.1 equiv. of cupric nitrate trihydrate failed to afford the tetranitro compound **3c**.

Table 1. Nitration of 2,7-di-*tert*-butyl-10b,10c-dimethyl-10b,10c-dihydropyrene **1a**

Run	$Cu(NO_3)_2 \cdot 3\ H_2O$/**1a**	Products (%)[a]
1	1.1	**1b** (75)[b]
2	2.1	**3a** (80)
3	3.1	**3b** (60)
4	4.1	**3c** (0)[c]

[a] Isolated yields are shown. [b] Starting compound **1a** was recovered in 20% yield. [c] Intractable mixture was obtained.

Interestingly, *ortho* dinitration was also observed in the case of nitration of the 4-methyl analog **4**, along with direct nitro substitution at the 4-methyl group. Thus, nitration of **4** with 3.1 equiv. of cupric nitrate trihydrate afforded 4,5-dinitro-9-nitromethyl-2,7-di-t-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (**5**) in 68% yield. To the best of our knowledge, nitration at the methyl group has not been observed previously in normal (benzenoid) aromatic systems by this nitrating system.

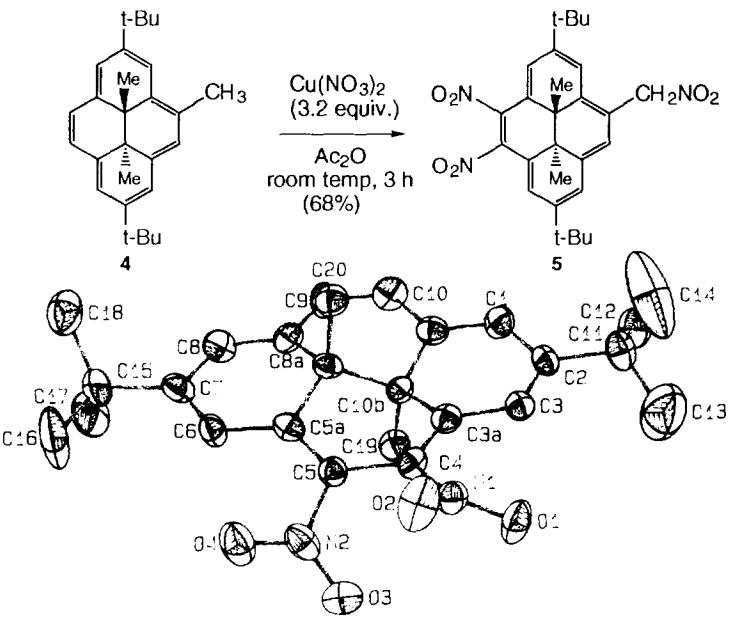
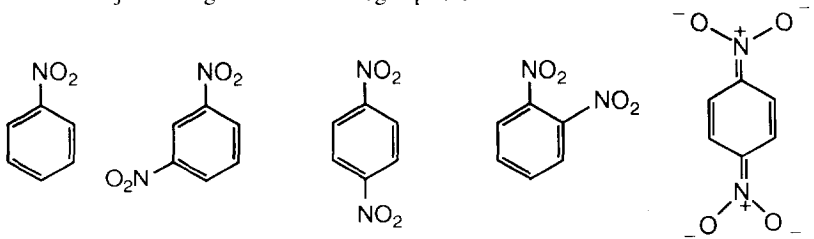


Figure 1. X-ray structure of 4,5-dinitro-2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (**3a**)

Electrochemistry. The availability of **3a**, an *ortho*-dinitro Hückel *4n+2* nonbenzenoid substance, suggested an interesting question: To what extent will the chemical properties of **3a** resemble those of *ortho*-dinitrobenzene? It appeared to us that a way to address this question would be to examine the electrochemical behavior of **3a**. Electrochemical experiments have been found useful in understanding the properties of nonbenzenoid hydrocarbons in general[1b] and this ring system in particular.[3] In order to understand the electrochemical behavior of **1b** and **3a**, it is necessary to review the behavior of analogous benzenoid species. In aprotic media nitrobenzene (**6**) undergoes one-electron reduction to a stable radical anion.[7] The first polarographic reduction wave of *meta*-dinitrobenzene (**7**) is 0.25 V positive of that of **6** (Table 2). This substantial shift (1 V = 23.06 kcal/mol) is due to the effect of the second inductively electron-withdrawing nitro group on the reduction potential of the first. The second reduction potential of **7**, on the other hand, is *negative* of the reduction potential of **6**. This is presumably because in the radical anion formed at the first step the first nitro group now bears a negative charge[8] and hence is inductively electron-supplying. *Para*- and *ortho*-dinitro benzenes (**8** and **9**), however, exhibit markedly different behavior. The first reduction potential of **8** is even more positive than that of **7**, even though the second nitro group in **8** is further away from the first than in **7** and should exert less of an inductive effect. Furthermore, the second reduction potential of **8** is *positive* of that of the reduction potential of neutral nitrobenzene, even though in the case of **8** one is reducing a species already carrying a negative charge. *Ortho*-dinitrobenzene (**9**) behaves similarly, although the effects are less dramatic. The anomalous voltammetric behavior of **8** and **9** (and other aromatic compounds bearing unsaturated groups *para* or *ortho* to each other)[9] has been ascribed[7,9] to quinoidal contributions such as **10** to the structure of the dianions and corresponding monoanion radicals, thus providing a means of charge localization and stabilization

in such species (presumably the effect is not as great in **9** because the two nitro groups are twisted somewhat out of planarity). The unusual ESR spectrum of the radical anion of **8** was also ascribed to a quinoidal contribution to the structure.[7] Compound **1b** exhibits a single one-electron wave at – 1.08 V, while **3a** exhibits two one-electron waves at – 0.88 and – 1.05 V.[10] This behavior is quite similar to that exhibited by *ortho*-dinitrobenzene (**9**); we conclude therefore that **3a** is reduced to a dianion in which quinoidal structure **11** is an important contributor to the resonance hybrid. The quinoidal structure **11** could be produced from **3a**, even though the two nitro groups are twisted out of the plane of the aromatic ring, because overlap is still largely preserved between the adjacent ring carbon and nitrogen pi-orbitals in the twisted structure.[11]



6 **7** **8** **9** **10**

Table 2. Reduction Potentials of Nitroarenes

Compound	$-E_1$ (V *vs* S. C. E.)	$-E_2$ (V *vs* S. C. E.)	Ref.
1b	1.08	---	this work
3a	0.88	1.05	this work
6	1.15	---	7
7	0.90	1.25	7
8	0.69	0.89	7
9	0.81	1.06	7

Computations. The conjecture that the dianion of **3a** is quinoidal is subject to computational test: to the extent that **11** represents its structure, the dianion of **3a** should exhibit a high degree of bond alternation, and the oxygen atoms should carry a higher negative charge than in neutral **3a**. The structure of **3a** and its corresponding dianion were computed by a modified Hückel molecular orbital method in which exchange and Coulomb integrals are adjusted in a reiterative process to fit computed pi-bond orders and electron densities, respectively (Table 3).[12] This method has been shown to fit the experimentally determined physical properties of hydrocarbon anions.[13] The lettering and numbering systems used for the ring bonds and atoms, respectively, of **3a** are shown below. Consider the computed pi-bond orders and electronic charges in the neutral substance **3a.** As expected for a resonance-stabilized ring system, the computations show that (a) the 14 carbon-carbon bonds all have about the same pi-bond order, (b) the carbon atoms all carry very little charge, and (c) the charge is evenly distributed around the ring (Table 3). The dianion, on the other hand, has a quite different computed structure. The computations show clear evidence for bond alternation between single and double bond character in $\mathbf{3a}^{-2}$ in the sense shown in structure **11**. As expected, the oxygen atoms of the dianion $\mathbf{3a}^{-2}$ are also computed to carry a higher degree of charge than in neutral **3a** (-0.56 per oxygen atom in the dianion *vs.* -0.37 per oxygen atom in neutral **3a**). Higher level (AM1) computations predict the same properties for $\mathbf{3a}^{-2}$.[14]

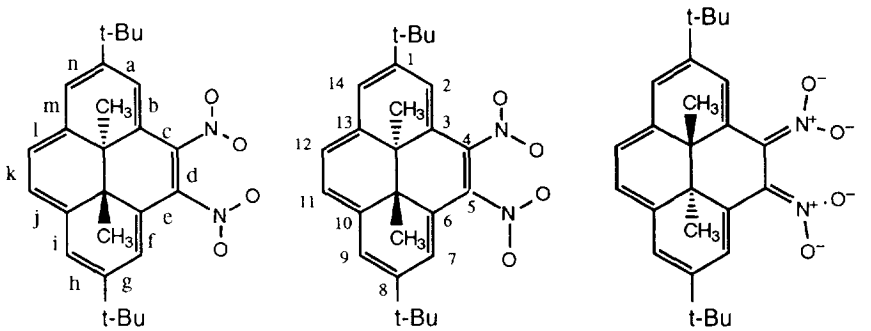


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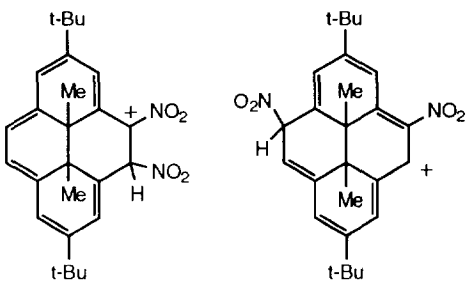
Table 3. Computed Structure of **3a** and the Corresponding Dianion[a]

Pi-Bond Orders

Bond:	a	b	c	d	e	f	g	h	i	j	k	l	m	n	C-N	N-O
3a	.63	.65	.62	.56	.62	.65	.63	.65	.64	.64	.64	.64	.64	.65	.32	.62
3a^{-2}	.55	.69	.60	.40	.60	.69	.55	.73	.51	.76	.49	.76	.51	.73	.47	.48

Atomic Charges[b]

Atom:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	N	O
3a	.01	.01	.01	.02	.02	.01	.01	.01	.01	.01	.01	.01	.01	.01	.67	-.37
3a^{-2}	-.03	-.10	-.03	-.10	-.10	-.03	-.10	-.03	-.08	-.04	-.05	-.05	-.04	-.08	.56	-.56



12 13

Orientation in Dinitration. The discovery that nitration of **1b** affords **3a** presents a mechanistic problem. Intermediate **12** (leading to **3a**) must be of lower energy than the corresponding structure **13** leading to **2**. Yet, the reasoning usually used to explain the fact that the nitro group is a *meta*-director in electrophilic attack upon nitrobenzene[15] predicts just the opposite: intermediate **12** forces positive charge to appear at the 4-position, whereas this is not the case in intermediate **13**. It is probably inappropriate, however, to extend benzenoid reasoning to [14]-annulenes, inasmuch as ions **12** and **13** both have more carbon atoms available to share the positive charge than do the corresponding intermediates in electrophilic attack upon nitrobenzene. The nitro group, although strongly electron-withdrawing, should have less effect upon the energy of these more highly charge-dispersed species. It may still seem surprising that the "ortho"-dinitration product (**3a**) should be formed in preference to the "para" (**1c**) or "meta" (**2**) substances, inasmuch as **3a** is more highly sterically hindered than either of the latter. In fact, however, there are a number of examples of *ortho*-dinitration in the literature. Dinitration of *p*-xylene is reported to afford primarily 2,3-dinitro-*p*-xylene together with a lesser amount of 2,6-dinitro-*p*-xylene,[16] the major product from dinitration of *p*-bromotoluene is 2,3-dinitro-4-

bromotoluene,[17] and very high *ortho:para* ratios (11-25:1) are found in the dinitration of benzene.[18] These results have been explained by coordination of the nitro group of the mononitro compound to the incoming nitronium group.[19] This could also explain the observed orientation in nitration of **1b** and **4**. It should also be noted that the highest *ortho:para* ratios in dinitration are found in non-polar solvents,[18] and the nitration of **1** is carried out in such a medium (acetic anhydride). A reviewer of this manuscript pointed out that it might well be that nitration by cupric nitrate is actually a radical process.[20] This would however still not explain the unusual regioselectivity of the nitration process, since radical-type nitrations are normally not regioselective.[20]

EXPERIMENTAL

General. Melting points are uncorrected. NMR spectra were measured at 270 MHz with a Nippon Denshi JEOL FT-270 spectrometer with Me_4Si as internal reference. *J*-values are given in Hz. IR spectra were measured for samples as KBr pellets or a liquid film on NaCl plates in a Nippon Denshi JIR-AQ2OM spectrophotometer. Mass spectra were obtained on a Nippon Denshi JMS-01SA-2 spectrometer at 75 eV. 2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene **1c** was prepared from toluene according to the reported procedure.[21] Preparation of 2,7-di-*tert*-butyl-4-methyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (**4**) was previously described.[22]

Nitration of 2,7-di-tert-butyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (1a). *Typical Procedure.* To a solution of 2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (**1a**) (200 mg, 0.58 mmol) in 40 mL of acetic anhydride held at 0° C was added powdered $Cu(NO_3)_2{\cdot}3H_2O$ (145 mg, 0.60 mmol). In about 10 min, the color of the solution had changed from deep green to deep brown. The mixture was stirred at room temperature (20° C) for 90 min before adding ice (10 g) and CH_2Cl_2 (40 mL). When the reaction of the acetic anhydride with water was complete, the CH_2Cl_2 layer was separated, washed with water, dried, and concentrated. The residue was taken up in CH_2Cl_2 and chromatographed over silica gel with hexane and benzene to give 40 mg of **1a** and 185 mg of deep brown solid. The deep brown solid was recrystallized from hexane to afford 4-nitro-2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene **1b** (170 mg, 75.2%) as deep brown prisms, mp 211-212 °C; IR (KBr) 3040, 2960, 1590, 1450, 1385, 1335, 1300, 1260, 1230, 1180, 960, 850, 770 cm^{-1}; ^1H NMR spectrum: see text; ^{13}C NMR spectrum: δ 14.962, 15.186, 29.400, 31.961, 31.754, 32.095, 35.994, 36.938, 118.077, 118.185, 122.049, 124.510, 124.582, 124.699, 126.963, 130.593, 134.429, 137.170, 138.311, 140.494, 147.628, and 153.503; mass spectrum : *m/z* 389 (M^+). Anal. Calcd for $C_{26}H_{31}NO_2$: C, 80.17; H, 8.02; N, 3.60. Found: C, 80.28; H, 8.08; N, 3.89. Compounds **3a** ,**3b**, and **5** were prepared in similar fashion:

4,5,9-Trinitro-2,7-di-tert-butyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (3b). Deep brown prisms (hexane-benzene, 3:1), mp 253-254°C; ^1H NMR spectrum: ^1H NMR spectrum: δ -2.98 (6H, s), 1.67 (9H, s), 1.68 (9H, s), 8.83 (1H, s), 9.00 (1H, d, J = 1.1), 9.02 (1H, d, J = 1.1), 9.30 (1H, s), and 9.43 (1H, s); ^{13}C NMR spectrum: δ 15.788, 15.878, 31.089, 31.691, 33.137, 36.947, 37.558, 118.455, 120.845, 123.261, 124.528, 128.149, 128.931, 130.198, 130.665, 135.463, 136.020, 136.352, 142.336, 155.157, and 157.744 (one peak is missing presumably because of peak overlapping); mass spectrum : *m/z* 479(M^+). Anal. Calcd for $C_{26}H_{29}N_3O_6$: C, 65.12; H, 6.10; N, 8.76. Found: C, 65.11; H, 5.10; N, 8.93.

4,5-Dinitro-2,7-di-tert-butyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (3a) Deep brown prisms (hexane-benzene, 3:1), mp 222-224°C; (lit.[2] 222-224 °C); IR (KBr) 3040, 2950, 1600, 1525, 1390, 1320, 1290, 1260, 875, 840, 790, 760, 750, and 670 cm^{-1}; ^1H NMR spectrum: see text; ^{13}C NMR spectrum: δ16.435, 31.080, 32.814, 36.875, 116.433, 124.376, 127.664, 130.341, 134.322, 140.503, and 155.597; mass spectrum : *m/z* 434 (M^+). Anal. Calcd for $C_{26}H_{30}N_2O_4$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.78; H, 6.99; N, 6.37.

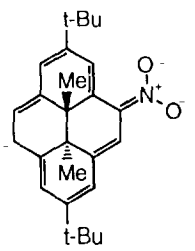
4,5-Dinitro-9-nitromethyl-2,7-di-tert-butyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (5). Deep brown prisms (hexane-benzene, 3:1), 68.0%, mp 216-218°C; ^{1}H NMR spectrum: δ -2.81 (3H,s), -2.78 (3H, s), 1.62 (9H, s), 1.63 (9H, s), 6.30 (1H, d, *J* = 13.4), 6.36 (1H, d, *J* = 13.4), 8.50 (1H, s), 8.53 (1H, s), 8.56 (1H, s), 8.86 (1H, d, *J* = 1.3), and 8.88 (1H, d, *J* = 1.3); mass spectrum : *m/z* 493 (M^+). Anal. Calcd for $C_{27}H_{31}N_3O_6$: C, 65.71; H, 6.33; N, 8.51. Found: C, 65.51; H, 6.40; N, 8.35.

X-Ray crystallographic determination. A crystal of **3a** (purple prism having approximate dimensions of 0.20 x 0.20 x 0.40 mm) was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Cu Kα radiation (λ = 1.54184 Å) on an Enraf-Nonius CAD4 computer-controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator. All calculations were carried out on a MicroVAX 3100 computer using MolEN (An Interactive Structure Solution Procedure, Enraf-Nonius, Delft, Netherlands, 1990). Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the settings angles of 25 reflections in the range 22°<θ <42° , measured by the computer-controlled diagonal slit centering method. The orthorhombic cell parameters and calculated volume are: a = 1962.0(2), b = 684.1(1), c = 1737.0(2) pm; α = 106.35°, β = 92.68°, γ = 72.36°; V = 2331.5 x 10^{-30} m^3. For Z = 4 and F. W. = 434.54, the calculated density is 1.24 g cm^{-3}. From the systematic absences of: h01:h=2n, 0k1:k=2n, and from subsequent least-squares refinement, the space group was determined to be Pna21 (No. 33). The data were collected at 23 °C using the ω-2θ scan technique. The scan rate varied from 5 to 20 °/min (in ω). A total of 8144 reflections were collected, of which 3949 were unique and not systematically absent. An empirical absorption correction based on a series of psi-scans was applied to the data. A secondary extinction correction was applied. The final coefficient, refined in least-squares, was 0.0000010. The structure was solved by direct methods (SIR88)[23] and difference Fourier syntheses. Using the 1840 reflections having intensities greater than 3.0 times their standard deviation, for 379 variable parameters, the structure was refined in full matrix least squares. Hydrogen atoms were located at calculated positions and included in the refinement with fixed isotropic thermal parameters (5.0 $Å^2$), but restrained to ride on the atom to which they are bonded. Atomic scattering factors were taken from a standard source.[24] The highest and lowest peaks in the final difference Fourier map each had heights of 0.36 e/$Å^3$. The parameters refined were atomic coordinates, temperature factors (anisotropic for carbon atoms), scale factor, and secondary extinction coefficient R = 0.061; R_w= 0.082. The refined atomic coordinates, temperature factors (anisotropic for carbon atoms), scale factors, and secondary extinction coefficients are available, on request, from the Cambridge Crystallographic Data Centre.

REFERENCES AND NOTES

1. (a) Snyder, J. P. *Nonbenzenoid Aromatics,* vol. 2, Academic Press: New York, 1971, pp. 1-166 ; (b) Fry, A. J.; "Electrochemistry of Nonbenzenoid Hydrocarbons". In *Topics in Organic Electrochemistry,* Fry, A. J.; Britton, W. E., Eds.,Plenum: New York, 1986, pp. 1-34.
2. Tashiro, M.; Yamato, T. *Organic Preparations and Procedures International,* **1982**, *14*, 216-219.
3. Fry, A. J.; Simon, J. A.; Tashiro, M.; Yamato, T.; Mitchell, T. R.; Dingle, T. W.; Williams, R. V.;Mahedevan, R. *Acta Chem. Scandinavica,* **1983**, *37B*, 445-450.
4. The [14]annulene system has been shown to be aromatic: Jug, K.; Fasold, E. *J. Amer. Chem. Soc.,* **1987**, *109*, 2263-2267.
5. (a) It is notable that *ipso* nitration (replacement of the t-butyl groups), which is frequently observed during nitration of reactive arenes,[5b,c] does not occur during the nitration of **1a**; (b) Tashiro, M.; Yamato, T.; Fukata, G.; Fukuda, Y. *J. Org. Chem.* **1981**, *46*, 2376-2379; (c) Moodie, R. B.; Schofield, K. *Acc. Chem. Res.* **1976**, *9*, 287-292; (d) Verboom, W.; Durie, A.; Egberink, R. J. M.; Asfari, Z.; Reinhoudt, D. N. *J. Org. Chem.* **1992**, *57*, 1313-1316..
6. Such effects are well documented in hindered nitroarenes (a) Fry, A. J.; "The Electrochemistry of Nitro Compounds". In *The Chemistry of Nitro and Azo Compounds,* S. Patai, Ed.;Wiley-Interscience, 1982,

p. 319; (b) Wheland, G. W.,*Theory of Resonance in Organic Chemistry,* Wiley: N. Y., 1945, p. 189.
7. Maki, A. H.; Geske, D. H. *J. Chem. Phys.*, **1960**, *33* , 825-832.
8. The negative charge in nitroarene radical anions is localized on the nitro group: a) Kemula, W.;Sioda, R. *J. Electroanal. Chem.* **1964**, *7,* 233-241; (b) Maki, A. H.; Geske, D. H. *J. Amer. Chem. Soc.*, **1961**, *83,* 1853-1860.
9. Kargin, Y.; Manousek, O.; Zuman, P. *J. Electroanal. Chem.* **1966**, *12,* 443-446.
10. Potentials were measured relative to 0.1 M $Ag/AgNO_3$ and converted to S.C.E. (see ref. 3).
11. Orbital overlap is proportional to $\cos^2\theta$, where θ is the dihedral angle between the two orbitals. Since $\theta = 16.1^\circ$ in **3a**, $\cos^2\theta = 0.92$, hence little overlap is lost by the twist of the nitro groups out of planarity.
12. Fry, A. J.; Fox, P. C. *Tetrahedron,* **1986**, *42,* 5255-5266.
13. Minsky, A.; Meyer, A. Y.; Hafner, K.; Rabinowitz, M. *J. Am. Chem. Soc.* **1983**, *105,* 3975-3981.
14. The computed properties of **7** and **8** and the corresponding dianions are unsurprising: (a) the pi-bond orders are almost identical in **7** and **8**, (b) $\mathbf{8}^{-2}$ exhibits a quinoidal structure with bond alternation, and (c) the dianion of **7** shows no evidence for quinoidal properties. Modified Hückel and AM1 computations, on the other hand, both suggested a considerably different structure for $\mathbf{2}^{-2}$. The minimum energy structure turned out not to have the expected C_{2v} symmetry; rather, the charge distribution and bond orders in the dianion are consistent with the unsymmetrical C_s structure ***i*** in which excess negative charge appears only on one nitro group. Interestingly,***i*** shows quinoid character, but of a considerably different character than in $\mathbf{3a}^{-2}$. The energy minimization for $\mathbf{2}^{-2}$ was started from a symmetrical C_{2v} structure, but it is possible that the C_s structure *i* is a local minimum, not the global minimum.



i

15. Gould, E. S., *Mechanism and Structure in Organic Chemistry,* Holt, Rinehart, and Winston, New York, 1959, pp. 412-440.
16. Kobe, K. A.; Levin, H. *Ind. Eng. Chem.*, **1950**, *42,* 352-358.
17. Kleene, R. D. *J. Amer. Chem. Soc.*, **1949**, *71,* 2259.
18. (a) Holleman, A. F. *Chem. Rev.*, **1924**, *1,* 197-230; (b) the major product is of course the *meta* isomer.
19. Hammond, G. S.; Modic; F. J.; Hedges, R. M. *J. Amer. Chem. Soc.* **1953**, *75,* 1388-1392.
20. (a) Ridd, J. H. *Chem. Soc. Rev.* **1991**, *20,* 149-165; (b) Kochi, J. K. *Adv. Phys. Org. Chem.* **1994**, *29,* 185-272.
21. Tashiro, M.; Yamato, T. *J. Am. Chem. Soc.* **1982**, *104,* 3701-3707.
22. Miyazawa, A.; Yamato, T.; Tashiro, M. *J. Org. Chem.* **1991**, *56,* 1334-1337.
23. Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Polidori, G. P.; Spagna, R.; Viterbo, D. *J. Appl. Crystallogr.* **1989**, *22,* 389-393.
24. Cromer, D. T.; Waber, J. T., *International Tables X-Ray Crystallography,* **1974**, *4,* 71-147.

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