

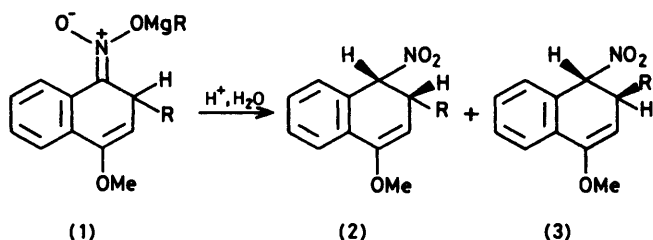
Stereochemistry of Protonation at Carbon of Nitronate Adducts from 1,6-Conjugate Addition of Grignard Reagents to 9-Nitroanthracenes. Crystal Structure of *cis*-9-Benzyl-10-nitro-9,10-dihydroanthracene

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Addition of RMgX (a, R = CH₃; b, R = PhCH₂) to 9-nitroanthracene (4) leads to formation of 1,6-adduct (5) in high yield. On treatment with dilute acetic acid, (5) is converted into the corresponding 10-alkyl-9,10-dihydroanthracene-9-nitronate anion (7), which quickly undergoes a stereoselective protonation at C-9 to give almost exclusively *cis*-10-alkyl-9-nitro-9,10-dihydroanthracene (8). Both (8a and b) remain unaltered under isomerization conditions. The formation of the more stable isomer, under kinetic control conditions, in a true boat system as (6), is interpreted in terms of a steric control on the proton approach, exerted by the axial alkyl group in position 10. The structure assignment of (8a, b) has been made by X-ray analysis of the benzyl derivative (8b). Structural parameters are discussed in comparison with those reported in the literature for analogous systems.

DURING our studies¹ on the reactivity of alkylcyclohexadienenitronate compounds formed by conjugate addition of RMgX to nitroarenes, we found² that the 1,4-addition product (1) undergoes a stereoselective protonation at carbon with preferential formation of the less

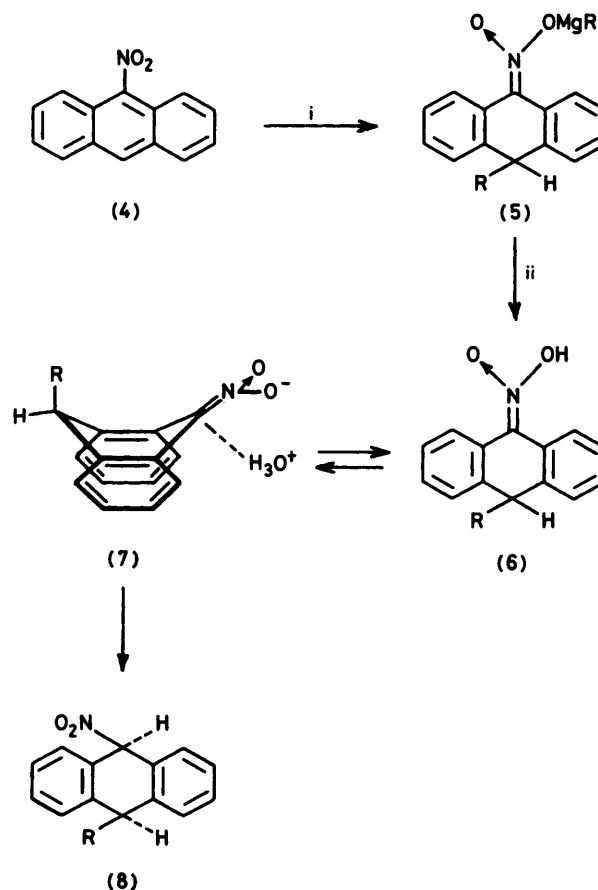


stable *cis*-isomer (2). In the 2-alkylcyclohexa-3,5-dienitronates (1) stereoselectivity is induced by the steric control³ exerted on prototropic approach by the axial alkyl group.⁴

In this work we report on protonation at carbon of the 4-alkylcyclohexa-2,5-dienitronate system, arising from 1,6-conjugate addition to 9-nitroanthracene (4). Treatment of (4) with an excess of RMgX gives the 9-alkylation adducts (5) in high yields. These reactions provide further evidence of the wide applicability of ring alkylation of nitroarenes^{2,5} by alkylmagnesium halides. However the anthracene substrate exhibits very low reactivity in comparison with mono-⁶ and bi-cyclic systems;⁷ longer times and a larger excess of RMgX [3 : 1 with respect to (4)] are required for reactions to go to completion. Treatment of a THF solution of (5) with dilute acetic acid (3%) leads to the almost exclusive formation of *cis*-10-alkyl-9-nitro-9,10-dihydroanthracene (8) through stereoselective protonation at carbon of the nitronate ion (7). No evidence of formation of *trans*-isomer could be obtained. Moreover compounds (8) remain unchanged under the isomerization conditions.³ Hence, in system (6) the formation of the more stable isomer is observed under kinetic control conditions.

A similar pattern has been reported in the case of

ethanoanthracene.⁸ In that very rigid system the formation of the more stable *trans*-isomer was accounted for by assuming that the reaction is controlled by the transition state, the geometry of which closely resembles the final products. A similar interpretation could also fit the present results: an attack *cis* to the alkyl group would involve a higher energy transition state owing to the steric interactions between the incipient equatorial



SCHEME Reagents: i, RMgX-THF; ii, HOAc-H₂O

nitro-group and the *peri*-hydrogens. However, in our opinion steric control by the alkyl group on the proton approach appears to be a more reasonable explanation. In the more stable conformation of (8), the alkyl group occupies the axial position so as to minimize steric interactions with the *peri*-hydrogens, and such arrangement causes the proton to approach from the less hindered opposite side (see Scheme).

This interpretation is in good agreement with the general features of the stereochemistry observed in non-rigid cyclic systems^{2,3,9,10} and suggests a transition state, whose geometry follows the Hammond postulate principles.

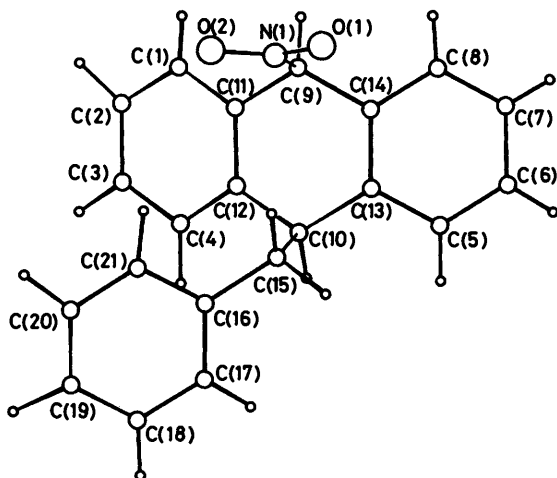


FIGURE 1 Projection of the structure of (8b) onto the plane determined by C(11)—C(14)

Structural Assignment. X-Ray Study of Compound (8b).—The homoallylic coupling constant between 9- and 10-H has been reported to be a useful tool for stereochemical assignment of 9,10-dihydroanthracenes.¹¹ Rabideau¹² and Marshall¹³ reported for a series of 9-alkyl and 9-carboxy-substituted anthracenes the following values: $J_{a-a} 2.0-2.5 > J_{a-e} 0.7-1.1 > J_{e-e} 0.4-0.55$ Hz. For (8) we found $J_{9,10}$ values of 0.6 Hz (see Experimental section). However, since in systems such as (8) the quantitative effect of the 9-nitro-substituent in lowering the homoallylic coupling constants is not known, the observed $J_{9,10}$ values cannot offer definite evidence for a *cis*-structure in (8) with hydrogens diequatorially arranged. The structural assignment has been made by means of X-ray analysis.

A projection of the molecule onto the C(11)—C(14) planar fragment of the central ring, and the numbering scheme used in the analysis are reported in Figure 1. Fractional co-ordinates for hydrogens and non-hydrogen atoms are reported in Table 1. Bond distances and angles are listed in Table 2.

This work represents the first example of an X-ray study on nitro-substituted 9,10-dihydroanthracenes. As shown in Figure 2, the nitro and the benzyl groups are in a 'boat-axial' conformation with respect to the central dihydrobenzene ring. The nitro-group is nearly

TABLE 1

(a) Fractional co-ordinates ($\times 10^4$) for non-hydrogens atoms with standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	4 074(3)	-1 444(4)	-1 745(8)
O(2)	5 010(4)	-2 483(3)	-1 371(9)
N(1)	4 678(3)	-1 780(3)	-952(7)
C(1)	6 446(3)	-2 172(3)	1 625(9)
C(2)	6 861(3)	-2 773(3)	2 760(9)
C(3)	6 372(3)	-3 132(3)	4 129(9)
C(4)	5 477(3)	-2 880(3)	4 400(8)
C(5)	3 161(3)	-553(2)	3 579(8)
C(6)	2 984(3)	313(2)	2 979(8)
C(7)	3 509(3)	687(3)	1 657(9)
C(8)	4 193(3)	183(2)	922(8)
C(9)	5 090(3)	-1 258(2)	643(8)
C(10)	4 062(2)	-2 026(2)	3 512(8)
C(11)	5 543(2)	-1 918(2)	1 850(8)
C(12)	5 046(2)	-2 276(2)	3 258(8)
C(13)	3 858(2)	-1 072(2)	2 863(8)
C(14)	4 359(2)	-704(2)	1 476(8)
C(15)	3 407(3)	-2 705(3)	2 597(9)
C(16)	3 547(2)	-3 685(2)	3 174(8)
C(17)	3 158(4)	-4 001(3)	4 687(10)
C(18)	3 301(5)	-4 883(4)	5 231(13)
C(19)	3 840(4)	-5 462(3)	4 299(12)
C(20)	4 227(4)	-5 160(3)	2 810(12)
C(21)	4 079(3)	-4 272(3)	2 211(10)

(b) Fractional co-ordinates ($\times 10^3$) for the hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	672(3)	-191(3)	69(7)
H(2)	755(4)	-292(3)	234(8)
H(3)	659(3)	-364(3)	484(7)
H(4)	510(3)	-315(3)	545(6)
H(5)	284(3)	-79(3)	463(7)
H(6)	249(3)	63(2)	350(6)
H(7)	342(3)	127(3)	135(6)
H(8)	456(4)	40(3)	3(9)
H(9)	553(3)	-91(2)	7(6)
H(10)	393(2)	-205(2)	475(6)
H(151)	344(3)	-271(3)	126(7)
H(152)	280(3)	-246(3)	299(7)
H(17)	278(4)	-360(4)	544(9)
H(18)	304(5)	-506(5)	641(10)
H(19)	407(4)	-613(4)	476(10)
H(20)	467(4)	-552(3)	197(9)
H(21)	436(5)	-396(5)	118(11)

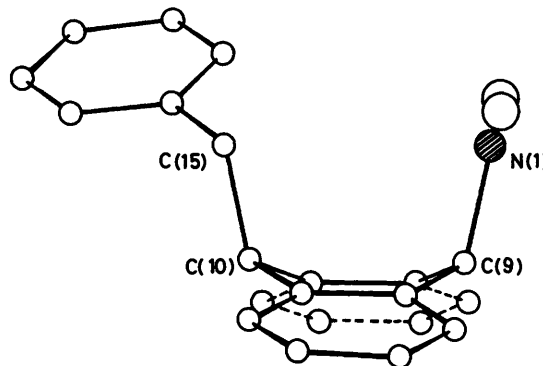


FIGURE 2 A view of the molecule (8b), showing the conformation of the central dihydrobenzene ring

perpendicular (75.2°) with respect to the least squares plane defined by C(11)—C(14), being its normal orthogonal to the C(11)—C(14) direction (92.6°) and it doesn't seem to influence the geometrical parameters of the anthracene skeleton, which are in good agreement with those found for other *cis*-9,10-dihydroanthracenes.

TABLE 2

Bond distances (Å) and angles (°), with estimated standard deviations in parentheses

(a) Bond distances			
O(1)-N(1)	1.179(7)	C(9)-C(14)	1.485(6)
O(2)-N(1)	1.181(7)	C(10)-C(12)	1.500(4)
N(1)-C(9)	1.557(7)	C(10)-C(13)	1.510(5)
C(1)-C(2)	1.375(8)	C(10)-C(15)	1.547(6)
C(1)-C(11)	1.385(5)	C(11)-C(12)	1.399(7)
C(2)-C(3)	1.370(8)	C(13)-C(14)	1.395(7)
C(3)-C(4)	1.378(6)	C(15)-C(16)	1.513(6)
C(4)-C(12)	1.392(7)	C(16)-C(17)	1.367(9)
C(5)-C(6)	1.371(5)	C(16)-C(21)	1.372(7)
C(5)-C(13)	1.384(6)	C(17)-C(18)	1.371(8)
C(6)-C(7)	1.381(8)	C(18)-C(19)	1.358(10)
C(7)-C(8)	1.364(7)	C(19)-C(20)	1.343(12)
C(8)-C(14)	1.386(5)	C(20)-C(21)	1.393(7)
C(9)-C(11)	1.489(6)		
(b) Carbon-hydrogen bonds			
C(1)-H(1)	0.90(5)	C(10)-H(10)	0.96(5)
C(2)-H(2)	1.08(6)	C(15)-H(151)	1.02(5)
C(3)-H(3)	0.97(5)	C(15)-H(152)	1.00(4)
C(4)-H(4)	1.05(5)	C(17)-H(17)	0.99(6)
C(5)-H(5)	0.99(5)	C(18)-H(18)	1.01(8)
C(6)-H(6)	0.95(4)	C(19)-H(19)	1.09(6)
C(7)-H(7)	0.89(4)	C(20)-H(20)	1.05(6)
C(8)-H(8)	0.92(6)	C(21)-H(21)	1.00(8)
C(9)-H(9)	0.93(4)		
(c) Bond angles			
O(1)-N(1)-O(2)	122.2(6)		
O(1)-N(1)-C(9)	119.1(5)		
O(2)-N(1)-C(9)	118.7(5)		
C(2)-C(1)-C(11)	121.1(5)		
C(1)-C(2)-C(3)	119.5(4)		
C(2)-C(3)-C(4)	120.6(5)		
C(3)-C(4)-C(12)	120.5(5)		
C(6)-C(5)-C(13)	121.0(4)		
C(5)-C(6)-C(7)	120.3(4)		
C(6)-C(7)-C(8)	119.7(4)		
C(7)-C(8)-C(14)	120.6(4)		
N(1)-C(9)-C(11)	109.7(3)		
N(1)-C(9)-C(14)	108.7(4)		
C(11)-C(9)-C(14)	114.2(4)		
C(12)-C(10)-C(13)	111.9(3)		
C(12)-C(10)-C(15)	112.4(3)		
C(13)-C(10)-C(15)	108.8(3)		
C(1)-C(11)-C(12)	119.5(4)		
C(1)-C(11)-C(9)	121.5(4)		
C(9)-C(11)-C(12)	119.0(3)		
C(4)-C(12)-C(10)	120.7(4)		
C(4)-C(12)-C(11)	118.8(3)		
C(10)-C(12)-C(11)	120.6(3)		
C(5)-C(13)-C(10)	121.6(3)		
C(5)-C(13)-C(14)	118.4(3)		
C(10)-C(13)-C(14)	120.0(3)		
C(8)-C(14)-C(9)	120.5(4)		
C(8)-C(14)-C(13)	120.0(3)		
C(9)-C(14)-C(13)	119.5(3)		
C(10)-C(15)-C(16)	113.1(4)		
C(15)-C(16)-C(17)	120.6(4)		
C(15)-C(16)-C(21)	120.9(4)		
C(17)-C(16)-C(21)	118.5(4)		
C(16)-C(17)-C(18)	120.6(6)		
C(17)-C(18)-C(19)	121.1(7)		
C(18)-C(19)-C(20)	118.8(5)		
C(19)-C(20)-C(21)	121.2(6)		
C(16)-C(21)-C(20)	119.7(5)		

The analysis of the planarity is reported in Table 3.

The dihedral angle between the least squares planes of the two benzene rings is 148.5° compared with 145° found in 9,10-dihydroanthracene,¹⁴ 147° in 9-*t*-butyl-9,10-dihydroanthracene,¹⁵ 152° in *cis*-9-methyl-10-ethyl-9,10-dihydroanthracene,¹⁶ 150° in bis(trimethylsilyl)-9,10-

dihydroanthracene,¹⁷ 155° in (+)-9-(3-dimethylamino-propyl)-10-methyl-2-trifluoromethyl-9,10-dihydroanthracene.¹⁸ Packing is consistent with van der Waals interactions.

TABLE 3

Analysis of planarity

(a) Distances ($\times 10^3$ Å) of relevant atoms from mean planes of the molecule with standard deviations in parentheses

Plane 1	C(11), C(12), C(13), C(14)
C(9)	347(5), C(10) 369(5), C(11) 5(5), C(12) -5.5, C(13), 5(5), C(14) -5.5
Plane 2	C(5), C(6), C(7), C(8), C(13), C(14)
C(5)	1(5), C(6) 13(5), C(7) -9(6), C(8) -12(5), C(13) -17(5), C(14) 21(5)
Plane 3	C(1), C(2), C(3), C(4), C(11), C(12)
C(1)	-3(5), C(2) -4(5), C(3) 9(5), C(4) -7(5), C(11) 2(4), C(12) 1(4)
Plane 4	C(16)-C(21)
C(16)	-4(4), C(17) 0(6), C(18) 9(8), C(19) -3(7), C(20) -7(7), C(21) 9(6)
Plane 5	C(9), C(11), C(14)
Plane 6	C(10), C(12), C(13)
Plane 7	O(1), O(2), N(1)

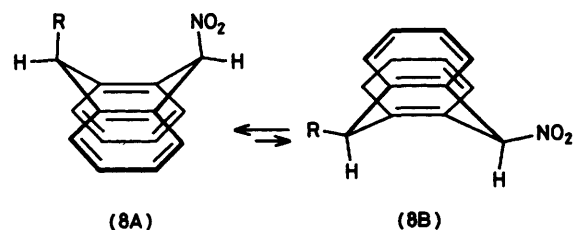
(b) Normal equations of planes in the form $lX + mY + nZ = p$ (X , Y , and Z are in Å, referred to orthogonal axes x , y , and z)

Plane	l	m	n	p
1	-0.4956	-0.5924	-0.6352	-3.2642
2	-0.6464	-0.3650	-0.6700	-4.5272
3	-0.2929	-0.7653	-0.5732	-1.0426
4	-0.8023	-0.3027	-0.5146	-3.7796
5	0.6733	0.6974	0.2458	3.8581
6	0.2146	0.3670	0.9051	2.6132
7	-0.6606	-0.4895	0.5692	-3.6666

(c) Dihedral angles (°) between planes

1-5, 25.5; 1-6, 26.0; 2-3, 148.5

Finally, when the *cis*-configuration is assigned to compounds (8) by means of the X-ray analysis of (8b), it appears from the $J_{9,10}$ value (< 0.6 Hz) for dihydroanthracenes (8) that the nitro and alkyl groups are diaxially arranged in conformation (8A). This assertion



is based on the hypothesis that in system (8) the nitro-group has little effect on the homoallylic coupling constants. On the other hand this effect was found to be negligible on vicinal coupling constants in cyclic systems.^{2,19}

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 257 instrument. ^1H N.m.r. spectra were recorded with a Varian 100 MHz spectrophotometer. All measurements were carried out in sealed vacuum-degassed solutions. Probe temperature was *ca.* 35 °C. THF was purified as previously

described.¹ The commercial 9-nitroanthracene (EGA Chemie) was crystallized from light petroleum-benzene.

10-Alkyl-9-nitro-9,10-dihydroanthracenes (8).—A solution of RMgX (60 mmol) in THF (20 ml) was added dropwise to a stirred solution of 9-nitroanthracene (20 mmol) in the same solvent (40 ml) at room temperature under nitrogen. The reaction was stirred for ca. 90 min and then added dropwise to a cold dilute acetic acid solution (5%) with stirring. The mixture was stirred for a few minutes and extracted with ethyl acetate. The organic layer was filtered from insoluble polymeric material, washed with a saturated solution of NaHCO₃, dried, and concentrated at reduced pressure to (5–10 ml). This solution was chromatographed on a silica gel column using 19:1 v/v cyclohexane-ethyl acetate as eluant to give (8a and b). Compound (8a) (72%) had m.p. 154–156 °C; ν (KBr) 1 550 and 1 360 cm⁻¹ (NO₂); δ (CDCl₃) 1.65 (3 H, CH₃, J_{10,CH_3} 7.5 Hz), 4.24 (1 H, H-10, $J_{9,10}$ < 0.6 Hz), 6.70 (1 H, H-9), and 7.20–7.70 (8 aromatic hydrogens) (Found: C, 75.35; H, 5.4; N, 5.8. C₁₅H₁₃NO₂ requires C, 75.3; H, 5.5; N, 5.85%). Compound (8b) (78%) m.p. 158–160 °C; ν (KBr) 1 555 and 1 355 cm⁻¹ (NO₂); δ (CDCl₃) 3.09 (2 H, CH₂, J_{10,CH_2} 8.0 Hz), 4.16 (1 H, H-10, $J_{9,10}$ < 0.6 Hz), 6.60 (1 H, H-9), and 6.83–7.67 (13 aromatic hydrogens) (Found: C, 80.0; H, 5.5; N, 4.5. C₂₁H₁₇NO₂ requires C, 80.0; H, 5.45; N, 4.45%).

Crystal Structure of 9-Benzyl-10-nitro-9,10-dihydroanthracene (8b).—Crystals, obtained from n-hexane, were prisms elongated on [001]. Lattice constants were determined using the CTDIF²⁰ program.

Crystal data. C₂₁H₁₇NO₂, $M = 315.4$. Orthorhombic, $a = 14.650(4)$, $b = 14.622(4)$, $c = 7.623(2)$ Å, $Z = 4$; $D_c = 1.28$ g cm⁻³, $U = 1 632.9$ Å³. Cu-K α radiation, $\lambda = 1.5418$ Å; μ (Cu-K α) = 6.2 cm⁻¹. Space group $Pca2_1$.

Intensity data were collected on a Siemens AED single-crystal diffractometer up to θ 70°. To collect every reflection the angles were determined on the basis of the orientation matrix and a measuring scan, along the θ circle, was made collecting the outline of the peak. 1 820 Independent reflections were measured, of which 1 034 were used in the crystal analysis, having intensities $> 2[\sigma^2 I + 10^{-4} I^2]^{\frac{1}{2}}$, where I is the relative intensity and $\sigma^2(I)$ its variance. The dimensions of the crystal specimen were 0.19, 0.24, and 0.33 mm. The effects of absorption were ignored.

Structure analysis and refinement. The structure was solved by direct methods by use of the SHELX programs.²¹ All non-hydrogen atoms were located from an E map calculated for phases of 303 reflections with $|E| > 1.2$. All atomic parameters were then refined (heavy atoms anisotropically and hydrogens isotropically) with full matrix least-squares cycles. The weighting function was of the form $1/w = \sigma^2(F_o) + 0.005F_o^2$. The final agreement factor R was 0.039 and R_w was 0.036. The atomic scattering

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1979, Index Issue.

factors for nitrogen, oxygen, and carbon were from ref. 22 and those for hydrogen from ref. 23.

Observed and calculated structure factors and thermal parameters are given in Supplementary Publication No. SUP 23295 (6 pp.).* All calculations were carried out on the CDC Cyber 76 of Consorzio per la Gestione del Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Bologna. Bibliographic searches were carried out using the Cambridge Crystallographic Data Files through the Servizio Italiano di Diffusione Dati Cristallografici, Parma.

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