Electron Spin Resonance Studies of Bicyclo[2.2.1]heptanes and Bicyclo[2.2.2]octanes Spin Labeled with Nitrobenzene Anion Radicals[1,2]

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Abstract: The esr spectra of a variety of bicyclo[2.2.2]octane and bicyclo[2.2.1]heptane systems spin labeled with nitrobenzene anion radicals have been analyzed and assigned almost completely. The large couplings of homo-para-exo hydrogens and the small couplings of homo-meta-exo hydrogens in 6-nitrobenzobicyclene systems show that the exo couplings are undoubtedly affected by the spin densities of the nitrobenzene ring. It was confirmed that the anti hydrogen couplings in 6,7-dinitrobenzonorbornene anion radical and 1,2,3,4-tetrahydro-1,4-methanonaphtho-6,7-semiquinone can be elucidated by the orbital symmetry theory. The increase of the anti and exo couplings by introduction of unsaturation at C-2–C-3, the existence of the $1,3-\pi,\pi$ interaction in the oxo-substituted nitrobenzobicyclene anion radicals, and the intramolecular electron exchange in some polynitro-substituted benzobicyclene anion radicals were clearly recognized.

Long range $\pi-\pi$ and $\pi-\sigma$ interactions have often been shown to play a major role in the chemistry of bridged bicyclic molecules. Since 1965, numerous electron spin resonance (esr) studies of rigid bicyclic systems having spin-labeling groups such as semi-dione,[3,4] *p*-semiquinone,[5,6] semifuraquinone,[7] dicyanoethylene anion radical,[8] nitroxyl,[9,10] and hydrazine cation radical[11] have been reported, and recently the esr spectra of many neutral radicals of rigid bicyclic compounds in the solid state[12,13] or solutions[14,15] have been investigated. The long-range hyperfine splittings in these spectra were remarkable and were discussed in relation to the stereochemistry. In relation to esr, the assignment of long-range coupling and the determination of signs of coupling constants in some radicals of these systems were established by means of

nmr[9] and the proton contact shift method.[16] All of these spin-labeled radicals except those labeled with the nitroxyl radicals have structures in which the spin-labeling groups are bounded by the two carbon atoms that are equivalent with respect to the symmetrical plane of the bridged bicyclenes. The nitrobenzene anion radical is one of the radicals whose esr spectra have been most investigated in detail both theoretically and experimentally.[17,18]

In this paper, we report an esr study of a variety of unsymmetrical 6-nitro-1,4-ethano-1,2,3,4-tetrahydronaphthalene (6-nitrobenzobicyclo[2.2.2]octene) and 6-nitro-1,2,3,4-tetrahydro-1,4-methanonaphthalene (6-nitrobenzonorbornene or 6-nitrobenzobicyclo[2.2.1]heptene) anion radical derivatives. The object was to explore the emphasized and selective long-range interactions compared with the symmetrical anion radicals reported previously. During this investigation, we prepared some oxo-substituted nitrobenzobicyclene anion radicals in order to establish the assignment of the couplings of parent radicals and to find the change of nitrogen couplings depending on the position of the oxo substituent. From their carbonium ion studies, Tanida, *et al.*,[19] reported homo-para interaction in the acetolysis of aromatic-substituted benzonorbornen-2(*exo*)-yl *p*-bromobenzenesulfonates. Russell, *et al.*,[3c] discussed the delocalization *via* $1,3-\pi,\pi$ overlap regarding olefinic and benzo derivatives of bicyclo[2.2.2]octane-2,3-semidione. Kosman and Stock[5b] reported that electron density is not transferred to the ethylenic π bond in bicyclic semiquinones, and explained the difference between semiquinones and semidiones in terms of spin transfer based on the symmetry rule. The tendency of the change of nitrogen couplings in oxo-substituted 6-nitrobenzobicyclene anion radicals will be of considerable interest to this problem.

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In the symmetrical norbornene anion radical system, the anti hydrogen atom lies on the symmetrical plane which bisects the spin-labeling component, and so the magnitude of the anti-C-9 hydrogen coupling constant can be explained by the orbital symmetry theory as described for the semidione[3f,g] and the semiquinone systems.[5] With this problem in mind, we examined the anti-C-9 hydrogen couplings of 6,7-dinitrobenzonorbornene anion radical, which is an antisymmetry system, and of 1,2,3,4-tetrahydro-1,4-methanonaphtho-6,7-semiquinone, which is a symmetry system, to confirm the symmetry theory.
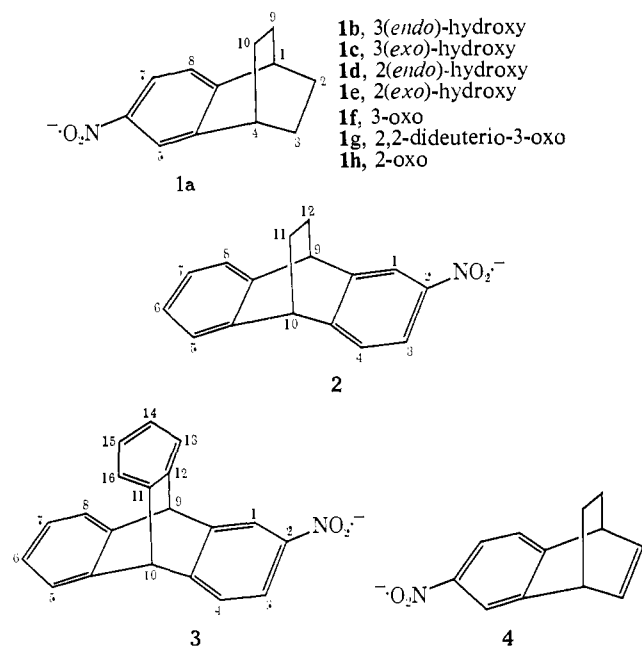
Finally, in the esr spectra of dinitro-substituted 9,10-ethano-9,10-dihydroanthracene (dibenzobicyclo[2.2.2]-octadiene) and 9,10-dihydro-9,10-methanoanthracene (dibenzobicyclo[2.2.1]heptadiene) anion radicals, we observed some interesting features which were considered to come from intramolecular electron exchange. Their exchange rates are discussed compared with several examples[20,21] of intramolecular electron transfer occurring between aromatic rings which are joined through saturated carbon chains or through oxygen or sulfur atoms.

Results

Nitro-substituted benzobicyclo[2.2.2]octene and benzonorbornene anion radicals and the related radicals were prepared in situ from the parent compounds by reduction with propiophenone enolate anion in DMSO containing potassium tert-butoxide.[22]

The esr spectrum of 6-nitrobenzobicyclo[2.2.2]-octene anion radical (1a) is shown in Figure 1. For the assignment of hyperfine splitting constants (hfsc) of 1a, seven other related compounds, 1b, 1c, 1d, 1e, 1f, 1g, and 1h, were also prepared (Chart I). They gave

Chart I

1b, 3(endo)-hydroxy
1c, 3(exo)-hydroxy
1d, 2(endo)-hydroxy
1e, 2(exo)-hydroxy
1f, 3-oxo
1g, 2,2-dideuterio-3-oxo
1h, 2-oxo

1a

2

3   4

well-resolved spectra under the same conditions. The hfsc of these anion radicals are listed in Table I, together with those of 2, 3, and 4.

The hfsc's of the nitrobenzene ring in 1a are similar

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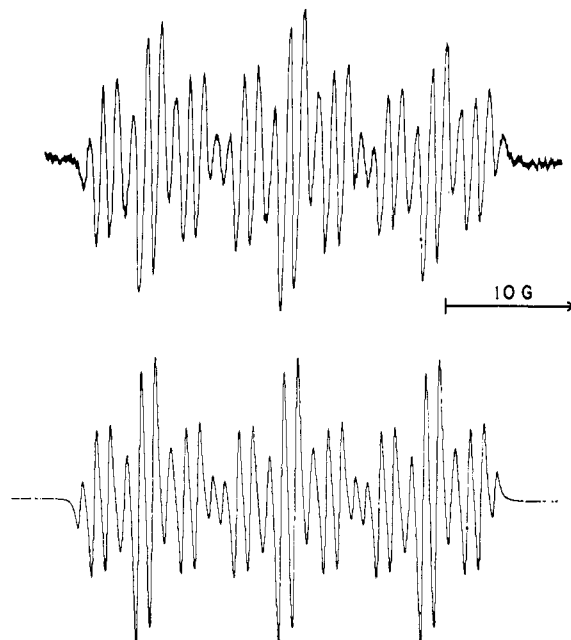
Figure 1. Esr spectrum of 6-nitrobenzobicyclo[2.2.2]octene anion radical (1a) in DMSO at 25°. The upper spectrum is experimental and the lower is a simulation based on the coupling constants given in Table I and Lorentzian line shapes.

Table I. Hyperfine Splitting Constants (gauss) for Nitrobenzobicyclo[2.2.2]octene Anion Radicals in DMSO at 25°

Radical	a^N	$a^H_{o(5)}{}^a$	$a^H_{o(7)}{}^a$	a^H_m	$a^H_{2,9\text{-exo}}$
1a	10.73	3.31	3.42	1.04	1.04 (2 H)
1b	10.76	3.31	3.41	1.02	1.02 (2 H)
1c	10.61	3.26	3.50	1.04	1.04 (2 H)
1d[b]	10.77	3.4	3.4	1.1	1.1 (2 H)
1e	10.53	3.30	3.41	1.08	1.08 (1 H)
1f[c]	10.20	3.31	3.48	1.09	1.09 (2 H)
1g[d]	10.24	3.32	3.49	1.09	1.09 (1 H)
1h	9.85	3.31	3.37	1.15	0.83 (1 H)
2	10.42	3.17 (C-1)	3.58 (C-3)	1.13	1.13 (1 H) (C-11)
3[e]	10.04	3.09 (C-1)	3.70 (C-3)	1.10	
4	10.66	3.17	3.55	1.17	1.17 (1 H)

[a] Assigned tentatively from the result of **9d**. [b] Unstable radical. [c] $a^H_{10\text{-exo}} = 0.17$, $a^H_{2,9\text{-endo}} = 0.17$ (2 H). [d] $a^H_{10\text{-exo}} = 0.17$, $a^H_{9\text{-endo}} = 0.17$, $a^D_{2\text{-exo}} = 0.17$. [e] The hfsc's in acetonitrile were described in E. G. Janzen and J. L. Gerlock, *J. Org. Chem.*, **32**, 820 (1967).

to those of nitrobenzene anion radical itself, although its a^N is 0.78 G larger than that of the latter (see **24a**), and the two ortho hydrogen atoms are not equivalent magnetically in 1a, and are assigned tentatively from the result for **9d**. In 1e the number of hydrogen atoms showing the coupling of 1.04 G in 1a decreased to 2 from 3. This means that two of the three hydrogen atoms of 1.04 G can be assigned to homo-para(C-2 and C-9)-exo hydrogen atoms. The couplings due to homo-meta(C-3 and C-10)-exo and homo-para-endo hydrogen atoms were not resolved in 1a, but in 1f, those of exo hydrogen atoms at C-10, and endo hydrogen atoms at C-2 and C-9, which were assigned on the basis of the spectrum of 1g, were observed. Coupling of benzene ring hydrogen atoms in 2 and 3, and of vinyl hydrogen atoms in 4 was either not observed or was less than 0.5 G in magnitude.

The results that coupling of hydrogen atoms at
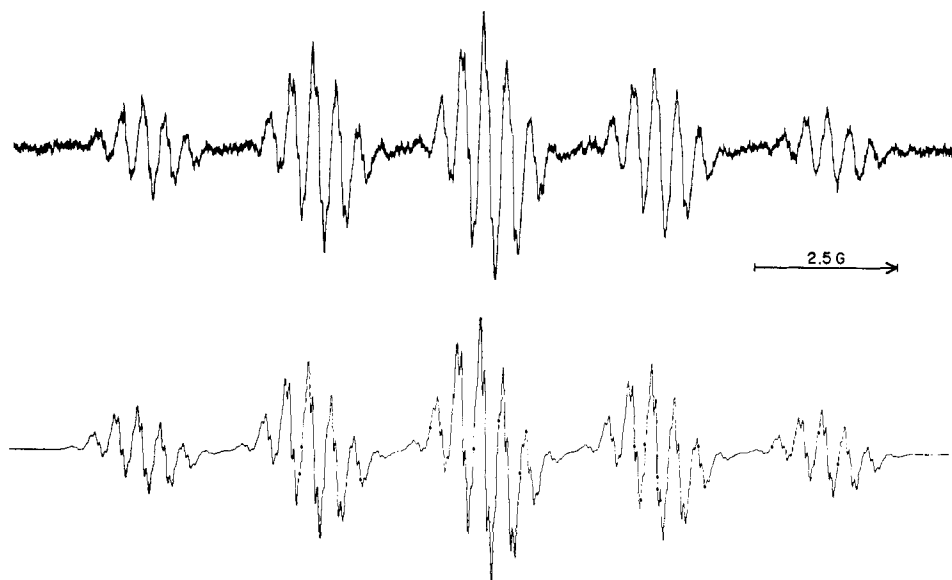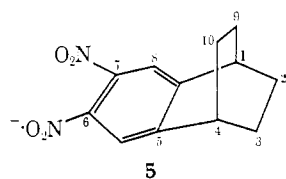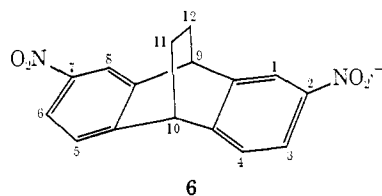
Figure 2. Esr spectrum of 6,7-dinitrobenzobicyclo[2.2.2]octene anion radical (5) in DMSO at 25°. The upper spectrum is experimental and the lower is a simulation based on the coupling constants given in Chart II and Lorentzian line shapes.
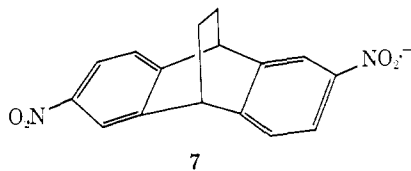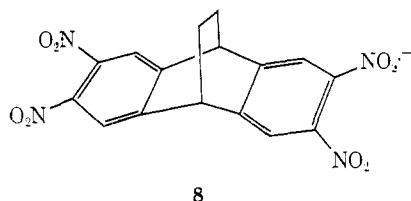
Chart II

$a^N = 3.03$ (2 N)
$a^H = 0.41$ (4 H); $H_{2\text{-}exo}$, $H_{3\text{-}exo}$, $H_{9\text{-}exo}$, $H_{10\text{-}exo}$
$a^H = 0.33$ (2 H); H_5, H_8
$a^H = 0.08$ (4 H); $H_{2\text{-}endo}$, $H_{3\text{-}endo}$, $H_{9\text{-}endo}$, $H_{10\text{-}endo}$

5

$a^N = 10.09$ (1 N)
$a^H = 1.7$ (2 H); H_3, H_6
$a^H = 1.6$ (2 H); H_1, H_8
$a^H = 0.52$ (4 H); H_4, H_5, H_{11} (2 H)

6

$a^N = 10.15$ (1 N)
$a^H = 3.50$ (1 H); H_3
$a^H = 3.25$ (1 H); H_1
$a^H = 1.16$ (2 H); H_4, H_{11} (1 H)

7

$a^N = 1.09$ (4 N)
$a^H = 0.18$ (8 H); H_1, H_4, H_5, H_8, H_{11} (2 H), H_{12} (2 H)
solvent: DMSO-t-BuOH (80:20)

8

bridgehead positions was not observed and that the hfsc's of exo hydrogen atoms were larger than those of endo hydrogen atoms are similar to those found for bicyclo[2.2.2]octane systems spin labeled with semi-dione,[3] semiquinone,[5] and semifuraquinone.[7] The most interesting point is that the homo-para-exo hydrogen couplings are considerably large but those of homo-meta-exo hydrogens are extremely small.

Dinitrobenzobicyclo[2.2.2]octene anion radical (5) and dinitro- and tetranitro-substituted dibenzobicyclo-[2.2.2]octadiene anion radicals (6, 7, and 8) were prepared in a similar manner to the mononitro-substituted ones (Chart II).

In 5, whose spectrum is shown in Figure 2, all the

couplings except those for two bridgehead hydrogen atoms were observed. Since the line width of the spectrum is very narrow (0.08 G), it is certain that the hfsc's of bridgehead hydrogen atoms are nearly equal to zero. The ortho hydrogen couplings in 6 and 7 were tentatively assigned from the result for 9d, and esr spectra of 6, 7, and 8 will be further discussed later.

The spectrum of 6-nitrobenzonorbornene anion radical (9a) is much more complicated than that of 1a, as shown in the previous paper.[1] In order to assign the hfsc's of 9a, its derivatives, 9b–12, were prepared (Chart III). Hfsc's of 3.66, 3.14, and 1.09 G were easily assigned to the benzene ring hydrogen atoms from the results for 1a and 9d: the hfsc of
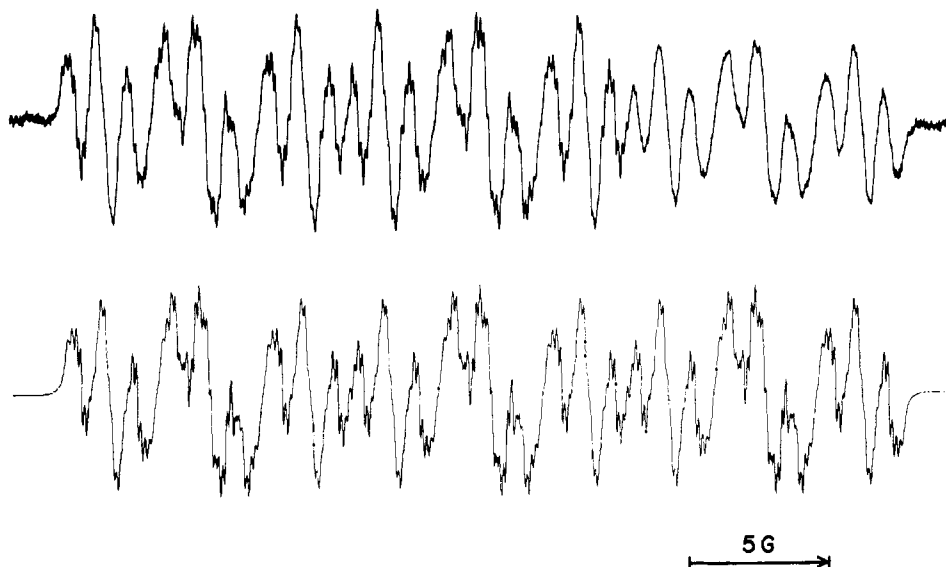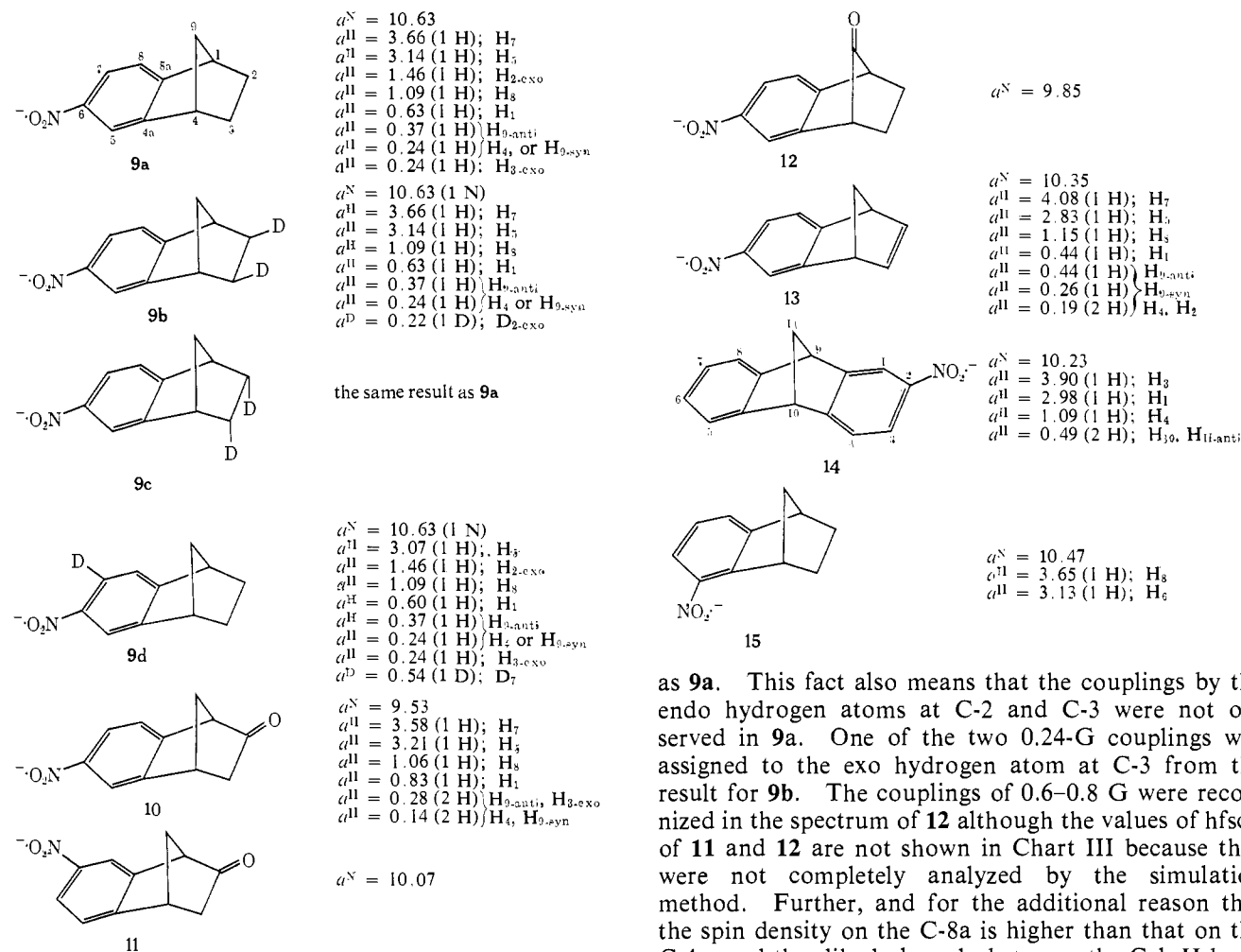
5 G

Figure 3. Esr spectrum of 6-nitrobenzonorbornen-2-one anion radical (10) in DMSO at 25°. The upper spectrum is experimental and the lower is a simulation based on the coupling constants given in Chart III and Lorentzian line shapes.

Chart III

9a

$a^N = 10.63$
$a^H = 3.66 (1\ H);\ H_7$
$a^H = 3.14 (1\ H);\ H_5$
$a^H = 1.46 (1\ H);\ H_{2\text{-exo}}$
$a^H = 1.09 (1\ H);\ H_8$
$a^H = 0.63 (1\ H);\ H_1$
$a^H = 0.37 (1\ H)\ H_{9\text{-anti}}$
$a^H = 0.24 (1\ H)\ H_4,\ \text{or}\ H_{9\text{-syn}}$
$a^H = 0.24 (1\ H);\ H_{3\text{-exo}}$

9b

$a^N = 10.63 (1\ N)$
$a^H = 3.66 (1\ H);\ H_7$
$a^H = 3.14 (1\ H);\ H_5$
$a^H = 1.09 (1\ H);\ H_8$
$a^H = 0.63 (1\ H);\ H_1$
$a^H = 0.37 (1\ H)\ H_{9\text{-anti}}$
$a^H = 0.24 (1\ H)\ H_4\ \text{or}\ H_{9\text{-syn}}$
$a^D = 0.22 (1\ D);\ D_{2\text{-exo}}$

9c

the same result as **9a**

9d

$a^N = 10.63 (1\ N)$
$a^H = 3.07 (1\ H);\ H_5$
$a^H = 1.46 (1\ H);\ H_{2\text{-exo}}$
$a^H = 1.09 (1\ H);\ H_8$
$a^H = 0.60 (1\ H);\ H_1$
$a^H = 0.37 (1\ H)\ H_{9\text{-anti}}$
$a^H = 0.24 (1\ H)\ H_4\ \text{or}\ H_{9\text{-syn}}$
$a^H = 0.24 (1\ H);\ H_{3\text{-exo}}$
$a^D = 0.54 (1\ D);\ D_7$

10

$a^N = 9.53$
$a^H = 3.58 (1\ H);\ H_7$
$a^H = 3.21 (1\ H);\ H_5$
$a^H = 1.06 (1\ H);\ H_8$
$a^H = 0.83 (1\ H);\ H_1$
$a^H = 0.28 (2\ H)\ H_{9\text{-anti}},\ H_{3\text{-exo}}$
$a^H = 0.14 (2\ H)\ H_4,\ H_{9\text{-syn}}$

11

$a^N = 10.07$

12

$a^N = 9.85$

13

$a^N = 10.35$
$a^H = 4.08 (1\ H);\ H_7$
$a^H = 2.83 (1\ H);\ H_5$
$a^H = 1.15 (1\ H);\ H_5$
$a^H = 0.44 (1\ H);\ H_1$
$a^H = 0.44 (1\ H)\ H_{9\text{-anti}}$
$a^H = 0.26 (1\ H)\ H_{9\text{-syn}}$
$a^H = 0.19 (2\ H)\ H_4,\ H_2$

14

$a^N = 10.23$
$a^H = 3.90 (1\ H);\ H_3$
$a^H = 2.98 (1\ H);\ H_1$
$a^H = 1.09 (1\ H);\ H_4$
$a^H = 0.49 (2\ H);\ H_{10},\ H_{11\text{-anti}}$

15

$a^N = 10.47$
$a^H = 3.65 (1\ H);\ H_8$
$a^H = 3.13 (1\ H);\ H_6$

3.14 G was attributed to the hydrogen atom at C-5, and accordingly that of 3.66 G to the hydrogen atom at C-7.

The coupling by the exo hydrogen atom at C-2 is undoubtedly 1.46 G from the results for **9b**, **9c**, and **10**, since in **9b** and **10** the coupling of 1.46 G disappeared and **9c** showed completely the same spectrum

as **9a**. This fact also means that the couplings by the endo hydrogen atoms at C-2 and C-3 were not observed in **9a**. One of the two 0.24-G couplings was assigned to the exo hydrogen atom at C-3 from the result for **9b**. The couplings of 0.6–0.8 G were recognized in the spectrum of **12** although the values of hfsc's of **11** and **12** are not shown in Chart III because they were not completely analyzed by the simulation method. Further, and for the additional reason that the spin density on the C-8a is higher than that on the C-4a, and the dihedral angle between the C-1–H bond and the p_z orbital on C-8a will be the same as that between the C-4–H bond and the p_z orbital on C-4a, the coupling of 0.63 G in **9a** was reasonably assigned to the hydrogen atom at C-1. The remaining coupling constants, 0.37 G (1H) and 0.24 G (1H), may be assigned to hydrogen atoms at anti-C-9, syn-C-9, or C-4; and we believe that the coupling by the anti hydrogen atom at
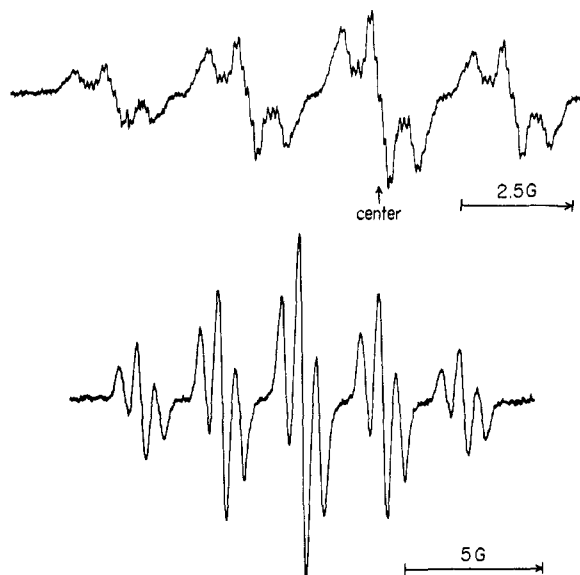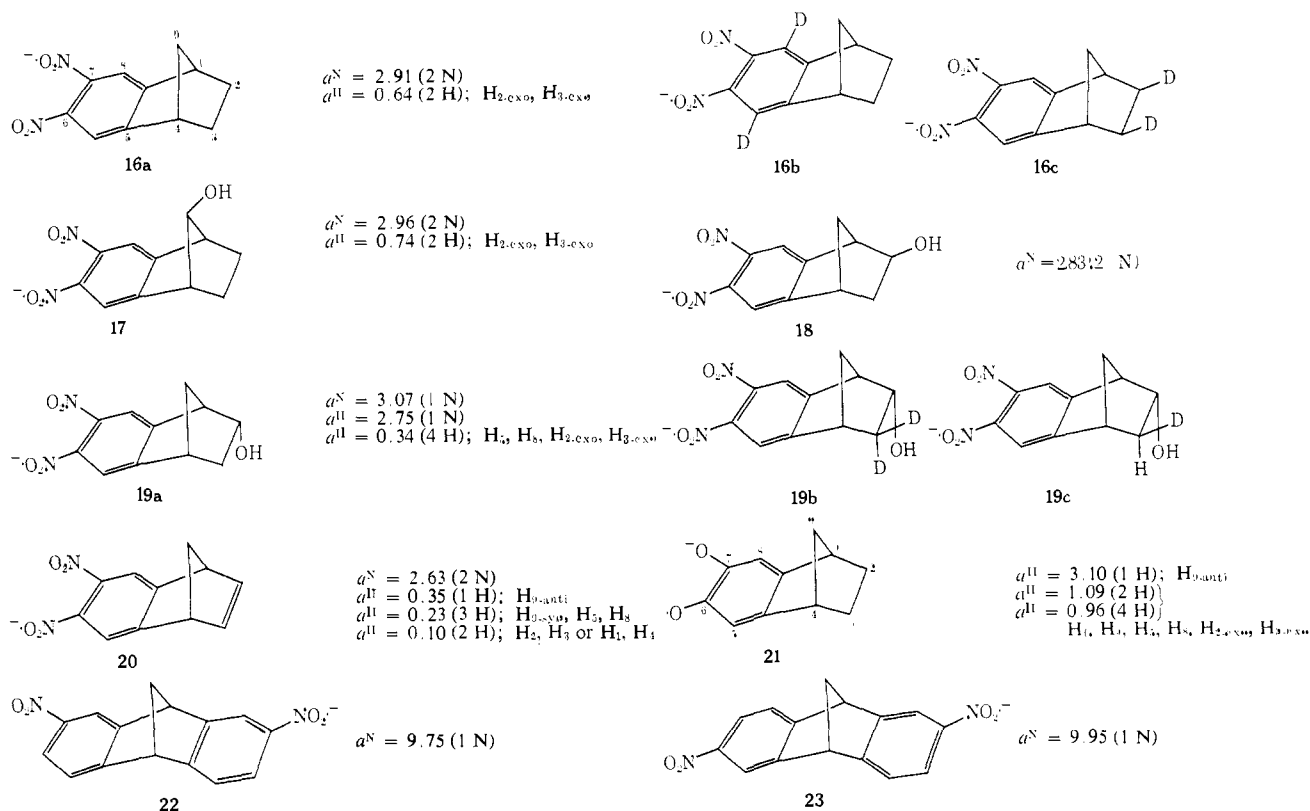
Figure 4. Esr spectra of 6,7-dinitrobenzonorbornene anion radical (16a) (top) and 5,8-dideuterio-6,7-dinitrobenzonorbornene anion radical (16b) (bottom) in DMSO at 25°. In the upper spectrum, the first (low field) four lines of the 1:2:3:2:1 quintet are reproduced.

assignments for **13** and **14** shown in Chart III can be made from the above results. Of interest is the finding that the value of the hfsc of the hydrogen atom at C-1 is considerably small. The analysis of the spectrum of **15** has not been established completely.

The spectrum of dinitrobenzonorbornene anion radical (**16a**) consisted of a quintet of triplets accompanied by small couplings below 0.4 G (see Figure 4). For the assignment of this spectrum, **16b** and **16c** were prepared. In **16b** the small couplings disappeared and the lines became sharp, while in **16c** the coupling of 0.64 G was not observed. Accordingly, the spectrum of **16a** was assigned as shown in Chart IV. The coupling by the anti hydrogen atom at C-9 is considered to be below 0.35 G because the spectrum of **17** shows almost the same pattern as **16a**, and in **19a** the couplings of hydrogen atoms at C-5 and C-8 are 0.34 G as confirmed from the results for **19b** and **19c**.

In the spectrum of **20**, hydrogen atoms at anti-C-9 and syn-C-9 should be responsible for the coupling of 0.35 or 0.23 G which resulted from the odd number of hydrogen atoms. It will be reasonable to assume that the larger one is the coupling of the anti hydrogen atom. The remaining two couplings of 0.23 G are

Chart IV

C-9 is 0.37 G from the result of proton contact-shift of 6-aminobenzonorbornene using bis(acetylacetonato)-Ni(II).[16] The above assignments are consistent with the results of Russell,[3] Stock,[5] Nelsen,[7] and their co-workers, and with those for **1a**.

In **10**, whose spectrum is shown in Figure 3, the assignments of two pairs of hydrogen atoms showing 0.28-G and 0.14-G couplings, respectively, are not conclusive. However, it may be presumed that the former are assigned to hydrogen atoms at anti-C-9 and exo-C-3, and the latter to those at syn-C-9 and C-4. The

probably due to hydrogen atoms at C-5 and C-8, from the results with **5** and **19a**. The radicals **22** and **23** will be discussed later in connection with **6**, **7**, and **8**. For comparison with **16a**, **21** was prepared and its esr measured. The assignments of couplings in **21** were not established completely, but the magnitude of hfsc of the anti hydrogen atom at C-9 is convincing.[1]

In order to evaluate the effects of the bicyclo[2.2.2]-octane and bicyclo[2.2.1]heptane rings on the nitrobenzene moiety, alkyl-substituted nitrobenzene anion radicals, **24b–27**, were prepared under the same con-

Table II. Hyperfine Splitting Constants (gauss) for Substituted Nitrobenzene Anion Radicals in DMSO at 25°

Radical	a^N	a^H_o	a^H_o	a^H_m	a^H_p	$a^H_{m'}$	$a^H_{p'}$
24a[a,b]	9.95	3.36	3.36	1.07	4.01		
24b	10.15	3.36	3.36	1.06	3.89	0.55	
24c[b,c]	10.42	3.37	3.37	1.10			1.86
24d	10.30	3.89	3.34	1.07			
24e	10.45	3.36	3.36	1.09			
24f	9.98	3.95	3.35	1.06			
24g	9.82	3.35	3.35	1.08			
24h	10.57	3.36	3.36	1.08		0.81	2.83
25a[b]	10.54	3.52	3.25	1.09		1.39	5.37
25b	10.48	3.41	3.35	1.09		1.66	6.46
26	10.61	3.70	3.07	1.06		1.33	5.10
27	10.54	3.56	3.34	1.11		1.47	5.79

[a] J. E. Harriman and A. H. Maki, *J. Chem. Phys.*, **39**, 778 (1963); $a^N = 9.87$, $a_o^H = 3.37$, $a_m^H = 1.07$, $a^H_p = 4.02$. [b] The hfsc's in other solvent are described in T. M. McKinney and D. H. Geske, *J. Amer. Chem. Soc.*, **89**, 2806 (1967). [c] $a^H_{CH_3} = 0.10$.

Chart V

24b, 3-CH(CH₃)₂   24f, 3-C(CH₃)₂COCH₃
24c, 4-CH(CH₃)₂   24g, 4-C(CH₃)₂COCH₃
24d, 3-C(CH₃)₂C₂H₅ 24h, 3,4-(CH₂CH₃)₂
24e, 4-C(CH₃)₂C₂H₅

25a, R = R' = H
b, R = R' = CH₃   26   27

cation radicals,[11] and the *o*-semiquinone **21** which was prepared to discuss the magnitude of the anti hydrogen coupling constant. In the nitrobenzobicyclenes, the

Table III. Exo (Anti) Hydrogen Coupling Constants (gauss)[a]

L·	![NO2]	![NO2 NO2]	![O- O-]	![O- O-]	![O- O-]	![O- O-]	H₃C CH₃[f] (—N—N—)·⁺
(norbornene)	1.04: $H_{p'x}$ 0.41 0.15: $H_{m'x}$			2.09	0.45	1.36	2.45
(bicyclooctene)	0.37: H_a <0.35: H_a 3.10: H_a 1.46: $H_{p'x}$ 0.64: H_x 1.09 or 0.96: H_x			6.54: H_a 2.43: H_x	0.70: H_a 0.70: H_x	1.03: H_a 0.37: H_x	1.7 or 3.0: H_a 4.78: H_x
(norbornadiene)	1.17			2.60	0.54		3.0
(bicyclooctadiene)	0.44 0.35			7.07[c] (Benzo) 0.80	1.41		2.07 or 1.34

[a] $H_{p'x}$, homo-para-exo H; $H_{m'x}$, homo-meta-exo H; H_a, anti H; H_x, exo H. [b] Reference 3a–c. [c] G. A. Russell, private communication. [d] Reference 5. [e] Reference 7. [f] Reference 11.

ditions. They gave well-resolved spectra and the coupling constants determined for them by the simulation method are shown in Table II, together with those for nitrobenzene anion radical itself (**24a**).

Discussion

Long-Range Coupling. The most characteristic point of the esr spectra of spin-labeled rigid bicyclene systems is the remarkable long-range coupling observed here and reported in the literature,[3–7] from which it may be concluded that the long-range interaction in these systems is attributed to a W-plan arrangement from the p_z orbital of the carbon atom having an odd electron to the C–H bonds of the bicyclene system. Further, the magnitude of long-range coupling was discussed semiquantitatively by Russell, *et al.*[3c–f] The exo and anti hydrogen coupling constants of mono- and dinitrobenzobicyclene anion radicals established here are given in Table III together with those of semidiones,[3] *p*-semiquinones,[5] semifuraquinones,[7] hydrazine
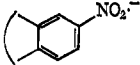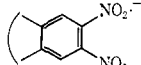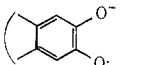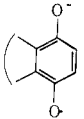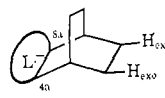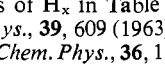
considerably large couplings by exo and anti hydrogen atoms can be explained apparently by the W-plan rule. The fact that the homo-para-exo hydrogen couplings in **1a** and **9a** are larger than are the homo-meta-exo hydrogen couplings gives evidence that the magnitudes of long-range interaction in the mononitrobenzobicyclenes are affected by the spin density at the para and meta positions of nitrobenzene anion radicals.

In the symmetrical norbornene anion radical system, the relative magnitude of the anti hydrogen coupling to the exo hydrogen coupling is large in the semidiones,[3] but equal in the *p*-semiquinones[5] and small in **16a**. Russell, *et al.*,[3] have elucidated the magnitude of the hfsc of anti hydrogen atom in the semidiones by the orbital symmetry theory. Since the anti hydrogen atom lies on the symmetrical plane which bisects the spin-labeling component, the opposite signs of the co-efficients (c_{4a} and c_{8a}) of the highest occupied molecular orbital for the ring juncture carbons in systems such as *p*-semiquinone[5] (antisymmetry) prevent delocalization

Table IV. Relative Spin Densities (%) of Exo Hydrogens[a]

L⁻		NO₂⁻	NO₂⁻/NO₂	O⁻/O·	O⁻/O·	quinone
	ρC-4a, C-8a	p: 0.069[b] m: 0.045[b]	0.07[b]	0.15[c]	0.25[d]	0.10[e]
H$_{exo}$ / H$_{exo}$	$\dfrac{\rho_{exo\text{-}H}}{\rho\text{C-4a, C-8a}}$	p': 1.21 m': 0.74	1.13		1.65	0.87
H$_{exo}$ / H$_{exo}$	$\dfrac{\rho_{exo\text{-}H}}{\rho\text{C-4a, C-8a}}$	p': 1.70 m': 1.05	1.77	1.43 or 1.26	1.96	1.35

[a] Hfsc's of H$_x$ in Table III are used: $\rho_{exo\text{-}H} = a^H_{exo}/508$; p', homo-para; m', homo-meta. [b] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963). [c] G. Vincow and G. K. Fraenkel, *J. Chem. Phys.*, **34**, 1333 (1961). [d] Reference 3a. [e] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **36**, 1944 (1962).

of the unpaired spin into the C-9 methylene position according to the equation[3g,23] $a^H = Q(c_{4a} + c_{8a})^2$ to show the relatively small coupling. In the cases of semifuraquinones,[7] dicyanoethylene anion radicals,[8] and hydrazine cation radicals[11] reported hitherto and in **16a** presented here, the anti-C-9 hydrogen couplings are also small compared with their exo hydrogen couplings because of the antisymmetry. In contrast, only the semidione system having the same signs shows a large coupling at the anti hydrogen atom. Examination of the esr of **21**, a new symmetry system other than the semidione system, has established a large anti hydrogen coupling as in the semidiones, providing an additional confirmation of the orbital symmetry theory. We conclude from these results that the symmetry theory is a general rule for the long-range interactions in a bridged bicyclene system. It is interesting to find a similar phenomenon in the carbonium ion chemistry of the benzonorbornene system: a strong rate enhancement was observed in the acetolysis of 6,7-dimethoxybenzonorbornen-9(anti)-yl p-bromobenzenesulfonate (an orbital symmetry type),[24] but not in that of the 5,8-dimethoxy derivative (an orbital antisymmetry type).[25,26]

In the case of the unsymmetrical anion radical, **9a**, the 8a (para) position has a large spin density value and the 4a (meta) position a small one of opposite sign. Accordingly, it is reasonable to consider that the magnitude of the hfsc by the anti hydrogen atom is small compared with that by exo hydrogen atom at C-2, mainly due to the partial cancellation of contribution from the 8a and 4a positions. The phenomenon that the exo or anti hydrogen coupling of these systems increases when unsaturation is introduced at C-2–C-3 (**1a** vs. **4** and **9a** vs. **13**) may come from increased strain in these systems as in the semidiones,[3] semiquinones,[5] semifuraquinones,[7] and hydrazine cation radicals[11] (see Table III).

(23) D. H. Whiffen, *Mol. Phys.*, **6**, 223 (1963).
(24) H. Tanida and H. Ishitobi, *J. Amer. Chem. Soc.*, **88**, 3663 (1966).
(25) G. A. Wiley, unpublished results cited in A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 389.
(26) The relative rate ratio of benzonorbornen-9(*anti*)-yl p-brosylate, its 6-methoxy derivative, and 6,7-dimethoxy derivative was 1:54:3000, and the ratio of benzonorbornen-9(*anti*)-yl p-brosylate and the 5,8-dimethoxy derivatives was 1:4. These different behaviors were discussed by Tanida, *et al.*[24]

The ratios of the spin densities on exo hydrogen atoms to those on the carbon atoms on the juncture (C-4a and C-8a) are summarized in Table IV together with the values for semidiones and semiquinones. The spin densities on exo hydrogen atoms are not always proportional to those on C-4a and C-8a; probably they are affected by the bond character between C-4a and C-8a. Thus, the conformational changes of the bicyclene systems due to the double bond character, aromatic ring character, or quinone character will bring the change in the extent of the spin delocalization.

Nitrogen Coupling Constants. Through investigation of the substituent effect on the hfsc of nitrobenzene anion radical derivatives, it is known that the nitrogen coupling constant (a^N) decreases with an electron-withdrawing group and increases with an electron-donating group.[27] The reciprocally proportional correlations between a^N and Hammett's σ constants and between a^N and absolute values of half-wave reduction potentials have also been reported.[28] The nitrogen coupling constants of **1a** and **9a** are larger than those of others shown in Table II. It is particularly interesting that the nitrogen coupling constant of **9a** is larger than that of **25b** which is the most suitable model compound, and that **1a** has the larger nitrogen coupling constant than **26** which, based on the results of **25a** and **25b**, probably has a similar coupling constant to the *cis*-dimethyl-substituted derivative of **26**.

The order of diminishing of the nitrogen coupling constant by the hydroxy substituent in the 6-nitrobenzobicyclo[2.2.2]octene anion radical series is unsubstituted ≃ homo-meta-endo ≃ homo-para-endo > homo-meta-exo > homo-para-exo. This result is of much interest in view of the result showing the large coupling by the exo hydrogen atom in this system, although the reason is not clear at this time.

Bridgehead Hydrogen Coupling Constants. In the bicyclo[2.2.2]octene system (**1** and **5**) no bridgehead hydrogen coupling was observed since the dihedral angle between the C$_\beta$–H bond and the p$_z$ orbital of the benzene ring is 90°. The introduction of unsaturation between C-2 and C-3 (**2** and **4**) must result in some deviation of their dihedral angles from 90°, but prob-

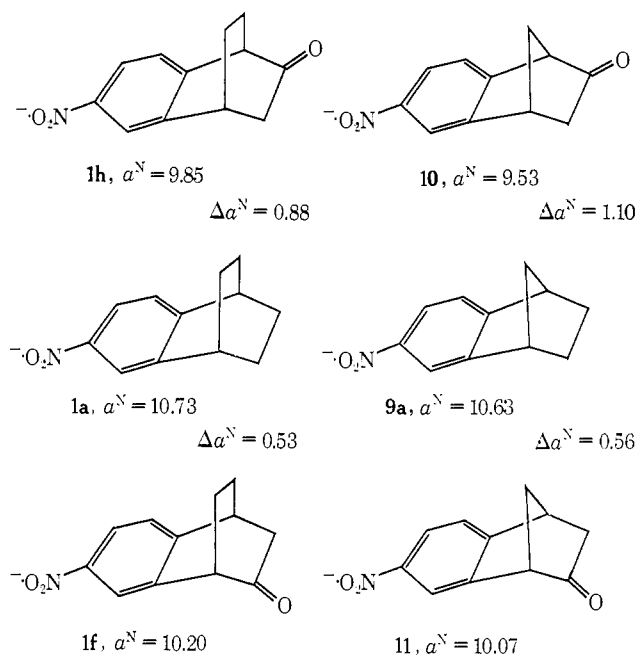(27) E. G. Janzen, *Accounts Chem. Res.*, **2**, 279 (1969), and references therein.
(28) A. H. Maki and D. H. Geske, *J. Amer. Chem. Soc.*, **83**, 1852 (1961).

ably to only a small extent because no β-hydrogen coupling could be observed in these systems.

In the bicyclo[2.2.1]heptene system, the bridgehead hydrogen atom shows hyperfine splitting because of the deviation from 90° of the dihedral angle. The magnitudes, however, are not the same. For example, the hydrogen atoms at C-1 in **9a**, **10**, and **13** show coupling values considerably different from one another as shown in Chart III. These may reflect slight changes of the bridgehead hydrogen conformations by the introduction of the 2-oxo group or the 2,3-double bond.
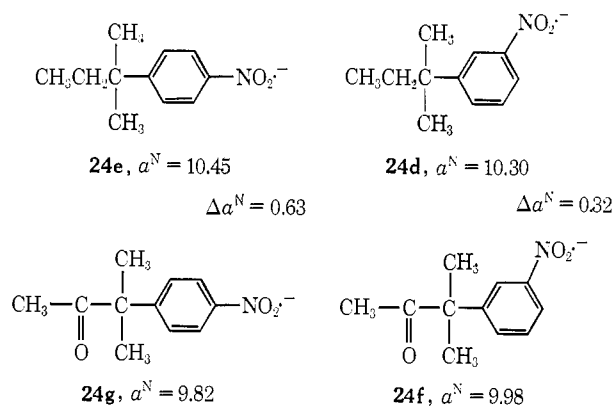
Homoconjugation in Homo-Para Ketones. In order to evaluate the effects of the oxo substituent on nitrogen coupling constants of nitrobenzobicyclo[2.2.2]-octene and nitrobenzonorbornene anion radicals, the values of nitrogen coupling constants of **1a**, **1f**, **1h**, **9a**, **10**, and **11** are listed in Chart VI and those of **24d**, **24e**,

Chart VI

1h, $a^N = 9.85$

$\Delta a^N = 0.88$

10, $a^N = 9.53$

$\Delta a^N = 1.10$

1a, $a^N = 10.73$

$\Delta a^N = 0.53$

9a, $a^N = 10.63$

$\Delta a^N = 0.56$

1f, $a^N = 10.20$

11, $a^N = 10.07$

24f, and **24g** as the model compounds[29] in Chart VII.

Chart VII

24e, $a^N = 10.45$

$\Delta a^N = 0.63$

24d, $a^N = 10.30$

$\Delta a^N = 0.32$

24g, $a^N = 9.82$

24f, $a^N = 9.98$

The homo-para ketones, **1h** and **10**, both show significant decreases in the nitrogen coupling constants compared with those of the homo-meta ketones **1f** and **11**. In the *tert*-amylnitrobenzene system the effects of the

(29) The best model compounds will be *sec*-butylnitrobenzene system, but α-acetylethylnitrobenzene anion radicals could not be prepared in this study, because carbanions were formed easily.
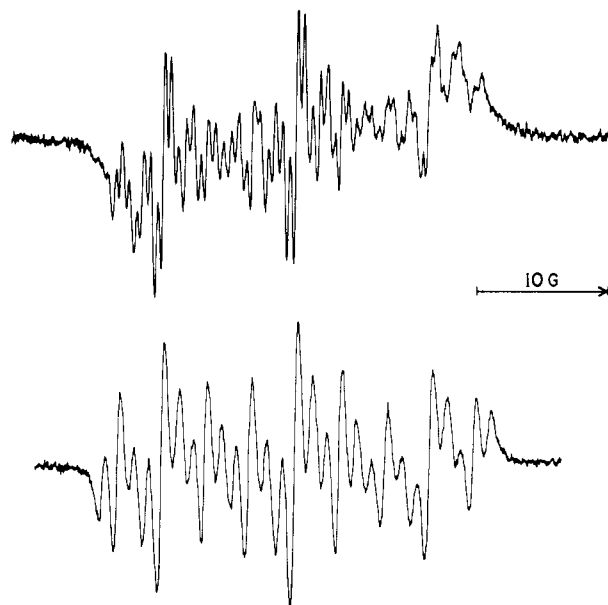

Figure 5. Esr spectra of 2,7-dinitro-9,10-ethano-9,10-dihydroanthracene anion radical (**6**) (top) and 2,6-dinitro-9,10-ethano-9,10-dihydroanthracene anion radical (**7**) (bottom) in DMSO at 25°.

oxo substituents on nitrogen coupling constants result in the decrease of 0.63 G in the para-substituted radicals and of 0.32 G in the meta-substituted radicals. These decreases can be ascribed to the electronegativity effect due to the β-carbonyl group. Accordingly, the differences between the bicyclene and the *tert*-amyl systems, i.e., $\Delta\Delta a^N$ (para) = 0.88 G − 0.63 G = 0.25 G and $\Delta\Delta a^N$ (meta) = 0.53 G − 0.32 G = 0.21 G in the bicyclooctene system, and $\Delta\Delta a^N$ (para) = 1.10 G − 0.63 G = 0.47 G and $\Delta\Delta a^N$ (meta) = 0.56 G − 0.32 G = 0.24 G in the bicycloheptene system, should be attributed to the 1,3-π,π interaction (or homoconjugation). The largest interaction in 2-oxo-6-nitro-benzonorbornene anion radical will be regarded as
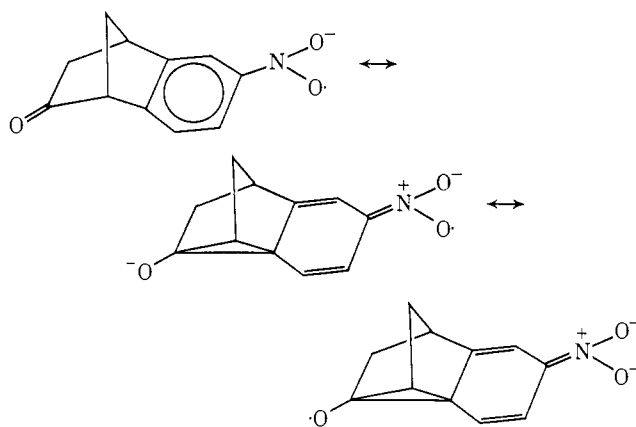

being due to the following homoconjugation. This result seems to correspond to the rate enhancement phenomena in the carbonium ion chemistry. Tanida, et al.,[19] observed that the rate enhancement by the homo-para-methoxy group in the acetolysis of aromatic-substituted benzonorbornen-2(*exo*)-yl brosylates at 77.6° was 178 times as large as that in the unsubstituted brosylate, while the homo-meta-methoxy group did not show any rate enhancement.

Ortho Hydrogen Coupling Constants. The two ortho

hydrogens in the nitrobenzene ring of the nitrobenzo-bicyclo[2.2.2]octene and nitrobenzonorbornene systems are not equivalent magnetically, as shown in Table I and Chart III, respectively, although the sums of their hfsc's are almost identical for each anion radical. We recognized experimentally that the larger coupling is attributed to the ortho hydrogen atom at C-7. In the nitrobenzobicyclene anion radicals, the order of the magnitudes of differences between the ortho hydrogen couplings is 1a (Δa^H_o = 0.11 G) < 2 (Δa^H_o = 0.41 G) < 9a (Δa^H_o = 0.52 G) < 3 (Δa^H_o = 0.61 G) < 14 (Δa^H_o = 0.92 G) < 13 (Δa^H_o = 1.25 G). This implies that the magnitude of difference between the two ortho hydrogens depends on the degree of strain in the nitrobenzene ring caused by the bicyclene moiety. In the monocyclic nitrobenzene system (see Table II), however, such a tendency was not noticed.

Electron Exchange Reactions. It is of interest that intramolecular electron exchange occurring between nitrobenzene rings which are separated by bicyclo[2.2.2]octane and bicyclo[2.2.1]heptane systems was found during the investigation of a variety of these anion radicals. In the spectrum of 6, we observed major couplings with two pairs of ortho and two meta hydrogen atoms, and with only one nitrogen atom (Figure 5). This fact can be explained in terms of the intramolecular electron exchange in this compound, having an exchange frequency 9.5 MHz $\leq \nu_{ex} \leq$ 28.2 MHz, as calculated from the values of nitrogen and larger ortho hydrogen coupling constants.

Several examples[30] of intramolecular electron exchange reactions have been reported between nitro-substituted aromatic rings that are joined through saturated carbon chains or through the oxygen or sulfur atom. For example, Harriman and Maki[20] recognized the electron exchange frequency of 2 MHz for 4,4'-dinitrobibenzyl anion radical, and that of greater than 100 MHz for bis(p-nitrophenyl)methane anion radical in DMSO at room temperature.

O_2N—〈 〉—X—〈 〉—NO_2

X = CH_2, CH_2CH_2, O, S

X = O, S
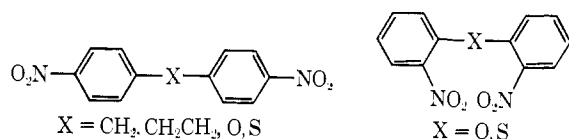
The hyperfine structure of 7 appears to result from couplings with the nucleus in only one benzene ring, so that the odd electron must be located in one nitrobenzene ring, or exchanges very slowly between two rings within the line width ($\nu_{ex} \leq$ 1.8 MHz). The odd electron of 8 couples with four nitrogen and four hydrogen atoms in both benzene rings equivalently, and the addition of a small amount of water to the DMSO–BuOH solution causes the line-width alternation. This suggests that a rapid inter-ring exchange (≥ 9 MHz) between the two dinitrobenzene rings occurs in this case. On increasing the base concentration in this experiment, the spectrum changes to a spectrum having a^N = 2.90 G (2 N), a^H = 0.49 G (2 H), and a^H = 0.24 G (2 H). In this case, line-width alternation was not observed and the electron exchange frequency, if any, is $\nu_{ex} \leq$ 0.7 MHz. Thus, this radical is different from 8, probably a trianion radical.

(30) See, for example, A. Hudson and G. R. Luckhurst, *Chem. Rev.*, **69**, 191 (1969).

The spectrum of 22 which is in similar situation to 6 shows major couplings with one nitrogen, four ortho hydrogen, and two meta hydrogen atoms. This would mean that the electron exchange between the two benzene rings occurs with 9.5 MHz $\leq \nu_{ex} \leq$ 27 MHz. On the other hand, the spectrum of 23, which is similar to 7, shows the major couplings with one nitrogen, two ortho hydrogen atoms of one nitrobenzene ring, and two meta hydrogen atoms in both nitrobenzene rings, though the resolution is not very good. It appears that the electron exchange of 23 proceeds with 3.1 MHz $\leq \nu_{ex} \leq$ 9.5 MHz, somewhat higher than that in 7, but somewhat lower than that in 22.

Furthermore, the esr spectra of dinitro- and trinitro-triptycene anion radicals shown in Chart VIII were

Chart VIII

28, $a^N = 9.77$

29, $a^N = 9.64$

30, $a^N = 9.47$

31, $a^N = 9.36$
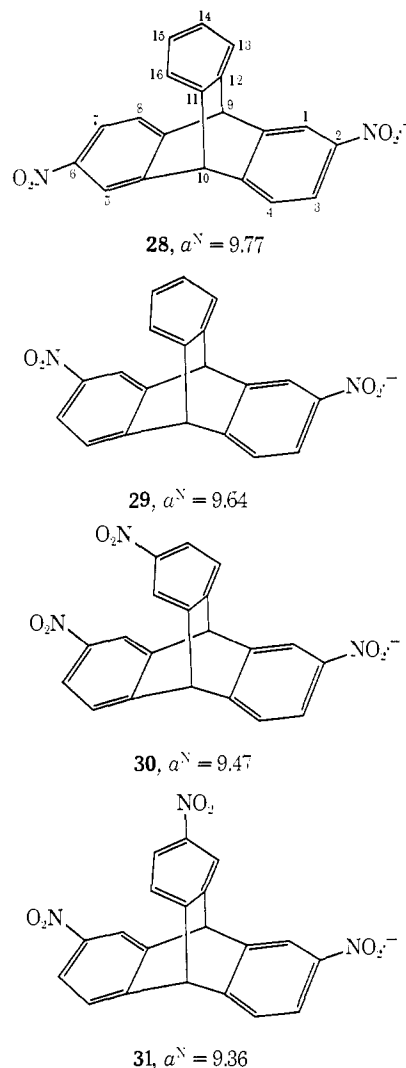
examined. All the spectra were so complicated that they were not analyzed completely, but the spectrum of 28 apparently showed an electron exchange reaction. This means that exchange is more facile in 28 than in 7. From the patterns of spectra for 28–31, it seems likely that the order of the frequency of electron exchange is 31 > 30 > 29 > 28.

We can interpret these phenomena in terms of intramolecular electron exchange attributable to a 1,3-π,π interaction as described above rather than to hyperconjugation for the nitro-substituted dibenzo-

bicyclo[2.2.2]octadiene system, because the bridgehead hydrogen atom of **7** lies on the plane of the benzene ring. In the dibenzobicyclo[2.2.1]heptadiene system, however, additional interaction due to hyperconjugation by the bridgehead methine group, which is located out of the plane of benzene ring, may exist.

Experimental Section

Esr Spectra. An inverted U-type mixing cell described by Russell, *et al.*,[22] was used for all experiments. About 0.5 ml of DMSO solution containing 0.004 *M* nitrobenzene derivative and 0.008 *M* propiophenone was placed in one arm of the mixing cell. Into another arm was placed *ca.* 0.5 ml of 0.016 *M* potassium *tert*-butoxide–DMSO solution. For the reduction reaction of *o*-dinitrobenzene derivatives, lower concentrations of potassium *tert*-butoxide than those for *o*-dinitrobenzenes were enough to prepare anion radicals. After degassing with commercial high purity argon for *ca.* 20 min, the mixing cell was inverted at room temperature (25°), and the reaction mixture was filled into a flat quartz cell. Spectra were recorded at room temperature on a Varian V-4502-15 X-band spectrometer with 100-kHz magnetic field modulation. Details of the calibration of magnetic fields and microwave frequencies and of spectral simulations have been described previously.[31] The *g* values found were 2.0047–2.0048 for para- and meta-substituted and meta,para-disubstituted nitrobenzene anion radicals, 2.0048–2.0050 for ortho-substituted nitrobenzene and *o*-dinitrobenzene anion radicals, and 2.0047 for **21**. Nitrogen coupling constants in this study are average values of at least three measurements. Hyperfine splitting constants other than that by nitrogen atoms were determined by spectral simulations.

Reagents.[32] **Dimethyl Sulfoxide.** Commercially available DMSO dried over calcium hydride was distilled twice under reduced pressure, passed through an active alumina column, then again distilled. Purified DMSO was stored under a nitrogen atmosphere.

Potassium *tert*-butoxide was purified by sublimation.

2,2′-Dideuterio-6-nitrobenzobicyclo[2.2.2]octen-3-one anion radical (1g) was obtained *in situ* from 6-nitrobenzobicyclo[2.2.2]octen-3-one in DMSO-d_6 solution containing potassium *tert*-butoxide and propiophenone.

6-Nitrobenzobicyclo[2.2.2]octadiene was prepared by the direct nitration of benzobicyclo[2.2.2]octadiene with acetyl nitrate in acetic anhydride at −10 to −20°. The nitro compound was isolated by preparative tlc and recrystallized from ligroin: mp 45°; pmr (CDCl₃) τ 1.93–2.12 (m, 2, C-5 and C-7 H), 2.68–2.83 (m, 1, C-8 H), 3.35–3.65 (m, 2, C-2 and C-3 H), 5.94 (broad s, 2, C-1 and C-4 H), 8.2–8.8 (m, 4, C-9 and C-10 H).

Anal. Calcd for C₁₂H₁₁NO₂: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.66; H, 5.53; N, 6.84.

2-exo,3-exo-Dideuterio-6-nitrobenzonorbornene was obtained from 2-*exo*,3-*exo*-dideuteriobenzonorbornene[33] by the same method as was used for the preparation of 6-nitrobenzonorbornene.[34] Pmr analysis showed that more than 90% exo hydrogen atoms were deuterated.

6-Nitro-7-deuteriobenzonorbornene was prepared from 6,7-dideuteriobenzonorbornene by the same method as mentioned above: pmr (CCl₄) τ 2.06 (s, 1, C-5 H), 8.77 (s, 1, C-8 H).

6,7-Dideuteriobenzonorbornene was prepared by the reduction of 6,7-dibromobenzonorbornene with tri-*n*-butyltin deuteride in benzene at 80°. Azobisisobutyronitrile was used as a radical initiator: pmr (CCl₄) τ 2.96 (s, 2, C-5 and C-8 H), deuterium content at C-6 and C-7 positions was more than 90%.

6,7-Dibromobenzonorbornene. Benzonorbornene was brominated with bromine (2 mol equiv) in the presence of a small amount of iron powder to give a mixture of bromo-substituted benzonorbornenes. The 6,7-dibromo derivative was produced as the major product together with monobromo- and tribromobenzonorbornenes as minor products. 6,7-Dibromobenzonorbornene

was isolated by repeated fractional distillations: bp 122–135° (0.6 Torr); pmr (CCl₄) τ 2.66 (s, 2, C-5 and C-8 H), 6.60–6.80 (m, 2, C-1 and C-4 H), 7.90–9.08 (complex m, 6).

Anal. Calcd for C₁₂H₁₀Br₂: C, 43.74; H, 3.34; Br, 52.92. Found: C, 43.82; H, 3.40; Br, 53.14.

6-Nitrobenzonorbornadiene was prepared by the direct nitration of benzonorbornadiene with acetyl nitrate in acetic anhydride at −5 to −10°. The distilled products contained five compounds, where 6-nitrobenzonorbornadiene was the major product (*ca.* 90%). The nitro compound was isolated by preparative glpc (5% Apiezon L on Chromosorb W; column temperature 200°), and distilled: mp 38.0–38.5°; pmr (CDCl₃) τ 1.95–2.22 (m, 2, C-5 and C-7 H), 2.73 (d, 1, *J* = 7.6 Hz, C-8 H), 3.07–3.35 (m, 2, C-2 and C-3 H), 5.93–6.10 (m, 2, C-1 and C-4 H), 7.46–7.85 (m, 2, C-9 H).

Anal. Calcd for C₁₁H₉NO₂: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.58; H, 4.91; N, 7.40.

2-Nitro-9,10-dihydro-9,10-methanoanthracene was prepared by the nitration of 9,10-dihydro-9,10-methanoanthracene with acetyl nitrate in acetic anhydride at 0°, and purified by preparative tlc: mp 118°; pmr (CDCl₃) τ 1.92 (d, 1, *J* = 2.0 Hz, C-1 H), 2.10 (doublet of doublets, 1, *J* = 2.0 and 8.0 Hz, C-3 H), 2.60–3.13 (m, 5, C-4, C-5, C-6, C-7, and C-8 H), 5.65 (t, 2, *J* ≃ 1.3 Hz, C-9 and C-10 H), 3.40 (t, 2, *J* ≃ 1.3 Hz, C-11 H).

Anal. Calcd for C₁₅H₁₁NO₂: C, 75.94; H, 4.67; N, 5.90. Found: C, 76.18; H, 4.48; N, 5.77.

9,10-Dihydro-9,10-methanoanthracene was synthesized from benzonorbornadiene and 1,4-dichlorobuta-1,3-diene by a similar method to that used for the preparation of 9,10-dihydro-9,10-methanoanthracen-11-one:[35] mp 158° (lit.[36] mp 154.5–155.5°).

Anal. Calcd for C₁₅H₁₂: C, 93.71; H, 6.29. Found: C, 93.67; H, 6.10.

5-Nitrobenzonorbornene[34] was obtained as a minor product in the nitration of benzonorbornene, and isolated by preparative glpc (Apiezon L 5% on Chromosorb W, column temperature 200°).

2-exo,3-exo-Dideuterio-6,7-dinitrobenzonorbornene was prepared from 2-*exo*,3-*exo*-dideuterio-6-nitrobenzonorbornene by the same procedure as was used for the preparation of 6,7-dinitrobenzonorbornene.[34] 5,8-Dideuterio-6,7-dinitrobenzonorbornene was obtained similarly from 5,6,7,8-tetradeuteriobenzonorbornene which was prepared by the deuteration of benzonorbornene (1.4 g) with D₃PO₄–BF₃ complex[37] (15.2 g) at room temperature. Twice repetition of the experiment gave more than 95% aromatic-deuterated benzonorbornene.

1,2,3,4-Tetrahydro-1,4-methanonaphtho-6,7-semiquinone radical (21) was prepared by the air oxidation of 6,7-dihydroxy-1,2,3,4-tetrahydro-1,4-methanonaphthalene (6,7-dihydroxybenzonorbornene) in a basic DMSO solution or by reduction of the corresponding *o*-quinone with the enolate anion of propiophenone in DMSO. 6,7-Dihydroxybenzonorbornene and the corresponding *o*-quinone were prepared by an analogous procedure to that used in the synthesis of 9(*anti*)-hydroxy-6,7-dimethoxybenzonorbornene.[24]

6-Acetoxy-7-methoxybenzonorbornene. 6-Methoxybenzonorbornene was acetylated at the C-7 position by Friedel–Crafts reaction with acetic anhydride and aluminum chloride in carbon disulfide at reflux temperature to yield a mixture of 6-acetyl-7-methoxybenzonorbornene and 6-acetyl-7-hydroxybenzonorbornene, the latter being predominant. The mixture was treated with methyl iodide and sodium hydride in dimethoxyethane to give the sole product, 6-acetyl-7-methoxybenzonorbornene: ir (CCl₄) 1674 cm⁻¹ (C=O). The compound was oxidized by the Baeyer–Villiger reaction with *m*-chloroperbenzoic acid in methylene chloride to give 6-acetoxy-7-methoxybenzonorbornene: mp 98°; ir (CCl₄) 1763 cm⁻¹ (C=O); pmr (CDCl₃) τ 3.16 (d, 2, spacing 1.5 Hz, C-5 and C-8 H), 6.22 (s, 3, OCH₃), 6.71 (broad s, 2, C-1 and C-4 H), 7.74 (s, 3, OCOCH₃), 8.0–9.05 (complex m, 6).

Anal. Calcd for C₁₄H₁₆O₃: C, 72.39; H, 6.94; O, 20.66. Found: C, 72.58; H, 7.08; O, 20.51.

6-Hydroxy-7-methoxybenzonorbornene was obtained by the hydrolytic reduction of 6-acetoxy-7-methoxybenzonorbornene with lithium aluminum hydride in ether: mp 40°; pmr (CDCl₃) τ 3.24 (d, 2, spacing 1.6 Hz, C-5 and C-8 H), 4.55 (s, 1, OH), 6.16 (s, 3, OCOCH₃), 6.73 (m, 2, C-1 and C-4 H), 8.0–9.1 (complex m, 6).

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Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.60; H, 7.23.

6,7-Dihydroxybenzonorbornene and 1,2,3,4-Tetrahydro-1,4-methanonaphtho-6,7-quinone. 6-Hydroxy-7-methoxybenzonorbornene (0.5 g) was treated with hydrobromic acid (1 ml, sp gr 1.48) in acetic acid (5 ml) at reflux temperature for 2 hr to give 6,7-dihydroxybenzonorbornene as the major product and the corresponding *o*-quinone as the minor one. They were separated by preparative tlc. 6,7-Dihydroxybenzonorbornene: mp 135–145°; pmr (CDCl₃) τ 3.29 (s, 2, C-5 and C-8 H), 5.08 (broad s, 2, OH), 6.77 (broad s, 2, C-1 and C-4 H), 8.0–9.1 (complex m, 6).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86; O, 18.16. Found: C, 75.25; H, 6.88; O, 17.96.

The *o*-quinone: red crystals, mp 71°; ir (CHCl₃) 1687 and 1667 cm⁻¹ (C=O).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.86; H, 5.72.

2,6-Dinitro- and 2,7-dinitro-9,10-dihydro-9,10-methanoanthracenes were obtained as an approximately 2:1 mixture by the nitration of 2-nitro-9,10-dihydro-9,10-methanoanthracene with acetyl nitrate in acetic anhydride at 0°. Both isomers were separated by preparative tlc. The 2,6-dinitro derivative had a higher R_f value than the 2,7-dinitro derivative (silica gel, petroleum ether–ether 1:2). The structural assignment was achieved by dipole moments. The 2,6-dinitro derivative (predominant isomer): mp 197°; pmr (CDCl₃) τ 1.85 (d, 2, $J = 2.0$ Hz, C-1 and C-5 H), 2.08 (doublet of doublets, 2, $J = 2.0$ and 8.0 Hz, C-3 and C-7 H), 2.54 (d, 2, $J = 8.0$ Hz, C-4 and C-8 H), 5.46 (t, 2, C-9 and C-10 H), 7.29 (t, 2, C-11 H); dipole moment (benzene), 4.55 D.

Anal. Calcd for $C_{15}H_{10}N_2O_4$: C, 63.83; H, 3.57; N, 9.93. Found: C, 63.54; H, 3.45; N, 9.85.

The 2,7-dinitro derivative: mp 204°; pmr (CDCl₃) almost identical with the 2,6-dinitro derivative; dipole moment (benzene), 5.93 D.

Anal. Found: C, 63.69; H, 3.66; N, 9.83.

m- and *p-*isopropylnitrobenzenes,[38] *m-* and *p-tert-*amylnitrobenzenes,[39] 5-nitroindane,[40] 6-nitrotetraline,[41] and 3,4-diethylnitrobenzene[42] were obtained by nitration of the corresponding hydrocarbons and isolated by preparative glpc.

3-(p-Nitrophenyl)- and 3-(m-nitrophenyl)-3-methylbutan-2-ones were prepared by the nitration of 3-methyl-3-phenylbutan-2-one together with the *o*-nitrophenyl isomer and isolated by preparative glpc (Apiezon L 5% on Chromosorb W, column temperature 200°): isomer ratio, ortho:metha:para $\simeq$ 3:1:5. para isomer: mp 89.5–90°; pmr (CDCl₃) τ 2.14 (A₂B₂ type m, 4), 8.03 (s, 3, COCH₃), 8.45 {s, 6, C(CH₃)₂}.

Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32; N, 6.76. Found: C, 63.72; H, 6.43; N, 7.09.

The meta isomer was not obtained pure, being contaminated with minor products.

4-Nitrobenzocyclobutene was prepared by the method described in the literature.[43]

Dinitro- and Trinitrotriptycenes. Triptycene (508 mg) in 15 ml of acetic anhydride was treated with 3 equiv of acetyl nitrate solution (10 *M*) in glacial acetic acid at 0° for 2 hr to give a mixture (550 mg) of nitrated triptycene. Five products were separated by preparative tlc (silica gel, CCl₄–ether 1:1). The yield of each product was as follows (in order of decreasing R_f value): the 2-nitro derivative, 150 mg; 2,6-dinitro, 140 mg; 2,7-dinitro, 200 mg; 2,6,14-trinitro, 30 mg; 2,7,14-trinitro, 10 mg. 2-Nitrotriptycene was identified by comparison of its pmr spectrum and melting point with those in the literature.[44]

2,6-Dinitrotriptycene. The nitration of this isomer gave only one trinitro isomer, which confirms the structure of this compound: mp >310° (lit.[44a] mp >350°); pmr (DMSO-d_6) similar to the reported spectrum.[44a]

Anal. Calcd for $C_{20}H_{12}N_2O_4$: C, 69.76; H, 3.51; N, 8.14. Found: C, 69.50; H, 3.23; N, 8.02.

2,7-Dinitrotriptycene was similarly identified by nitration, which gave a mixture of two isomeric trinitrotriptycenes in comparable amounts: mp 265°; pmr (DMSO-d_6) τ 1.65 (d, 2, $J = 2.0$ Hz, C-1 and C-8 H), 1.99 (doublet of doublets, 2, $J = 2.0$ and 8.0 Hz, C-3 and C-6 H), 2.25 (d, 2, $J = 8.0$ Hz, C-4 and C-5 H), 2.28–2.97 (A₂B₂ type m, 4. C-13, C-14, C-15, and C-16 H), 4.79 (s) and 4.85 (s) (2, C-9 and C-10 H).

2,6,14-Trinitrotriptycene was identified in the same way. This compound was the sole product of nitration of the 2,6-dinitro isomer: mp 180°; pmr (DMSO-d_6) τ 1.58 (d, 3, $J = 2.0$ Hz, C-1, C-5, and C-13 H), 1.90 (doublet of doublets, 3, $J = 2.0$ and 8.0 Hz, C-3, C-7, and C-15 H), 2.17 (d, 3, $J = 8.0$ Hz, C-4, C-8, and C-16 H), 3.57 (s, 2, C-9 and C-10 H).

2,7,14-Trinitrotriptycene: mp >310°; pmr (DMSO-d_6) τ 1.57 (d, 3, $J = 2.0$ Hz, C-1, C-8, and C-13 H), 1.92 (doublet of doublets, 3, $J = 2.0$ and 8.2 Hz, C-3, C-6, and C-15 H), 2.17 (d, 3, $J = 8.2$ Hz, C-4, C-5, and C-16 H), 3.53 (s) and 3.60 (s) (2, C-9 and C-10 H).

Anal. Calcd for $C_{20}H_{11}N_3O_6$: C, 61.72; H, 2.85; N, 10.80. Found: C, 61.80; H, 2.98; N, 10.74.

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