

Cyclopropane–Arene Interactions. II. Intramolecular Charge Transfer and Geometry Effects in Cyclopropyl Nitroaromatic Systems

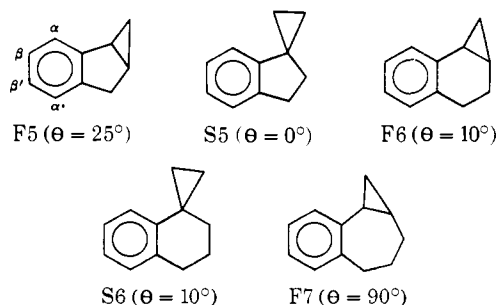
Roger C. Hahn,* Philip H. Howard, and George A. Lorenzo¹

Contribution from the Department of Chemistry, Syracuse University, Syracuse, New York 13210. Received March 5, 1971

Abstract: The ultraviolet spectra have been obtained of 2- and 5-nitro-1,1a,6,6a-tetrahydrocycloprop[*a*]indenes (α - and α' -NO₂-F5), 7'- and 4'-nitrospiro(cyclopropane-1,1'-indans) (α - and α' -NO₂-S5), 7- and 4-nitro-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalenes (α - and α' -NO₂-F6), 8'- and 5'-nitrospiro(cyclopropane-1,1'-tetralins) (α - and α' -NO₂-S6), 8- and 5-nitro-1,1a,2,3,4,8b-hexahydrobenzo[*a*]cyclopropa[*c*]cycloheptenes (α - and α' -NO₂-F7), and selected reference compounds. In contrast with the spectra of β - and β' -nitro isomers, these spectra show alicyclic ring size effects. Spectra of α - and α' -nitro systems, in which nitro and cyclopropyl are ortho and meta, respectively, to one another, are similar to one another and different from β' -nitro isomer spectra (nitro and cyclopropyl para); cyclopropane geometry effects appear in *m*-nitrocyclopropyl systems. These phenomena are interpretable through generalization of published molecular orbital calculations involving first excited states. Evidence is presented for charge-transfer character in these spectra, and for severe steric hindrance in some *o*-nitrocyclopropyl compounds.

It was previously established that interaction of a cyclopropane ring with an attached *p*-nitrobenzene system is a function of cyclopropane geometry, detectable in the ultraviolet spectra of a variety of fixed-geometry *p*-nitroaryl cyclopropanes.² However, features of some of the uv spectra obtained at that time suggested that a full description of structure–spectra relationships was not yet in hand for cyclopropylaromatic systems. Therefore, the work was extended to include uv spectra of *all* aryl nitro derivatives of the initially studied systems; the picture emerging is presented here.

The hydrocarbon systems used in the initial study and in the present one were 1,1a,6,6a-tetrahydrocycloprop[*a*]indene (F5), spiro(cyclopropane-1,1'-indan) (S5), 1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalene (F6), spiro(cyclopropane-1,1'-tetralin) (S6), and 1,1a,2,3,4,8b-hexahydrobenzo[*a*]cyclopropa[*c*]cycloheptene (F7);³ θ (see below) may be considered the angle of departure of the cyclopropane ring from ideal geometry for conjugation with the adjacent π system.²



Bathochromic λ_{\max} shifts in the single, intense long-wavelength band observed in the β' -nitro series (F7 < F5 < F6 \approx S6 < S5) (Figure 1) were attributed to increasingly favorable cyclopropane geometry for con-

jugative interaction with the *p*-nitrobenzene moiety; the conclusion with respect to the preferred cyclopropane geometry was in accord with the bulk of published theories and experiments.⁴ Insofar as one can consider cyclopropane electron delocalization in a “classical” manner,⁵ results in the above series appeared to be interpretable in terms of classical resonance interaction between the cyclopropyl group and the nitrobenzene system, with varying degrees of steric inhibition of that interaction.

As part of the initial study, the uv spectra of the β -nitro derivatives of F5, S5, etc., also were obtained² (Figure 2) to demonstrate the insensitivity of the nitrobenzene chromophore to the presence or geometry of a *m*-cyclopropyl group. However, in addition to the intense long-wavelength “cyclopropane-insensitive” band seen in all of these spectra, most contained a weaker, longer wavelength band apparently affected by the geometry of the cyclopropyl group. For β -NO₂-F7, with the worst cyclopropane geometry for conjugative interaction ($\theta \approx 90^\circ$), this band was not detectable, while it was most prominent for β -NO₂-S5 ($\theta = 0^\circ$). Intermediate cyclopropane geometries (β -NO₂-F5, F6, S6) corresponded to bands of intermediate prominence. Partial merging of this band with the higher energy one in all cases made λ_{\max} and ϵ_{\max} assignments approximate, and the possibility remained that both the energy and the intensity of the longer wavelength transition were affected by cyclopropane geometry.

Tentative rationalization of the differences in β - and β' -nitro derivative spectra started with the assumption that the transitions involved have considerable charge-transfer (CT) character. Nitrobenzene itself has absorption bands (hexane) at 252 (intense) and 283 $m\mu$ (weak), which have been assigned as π - π^* (1L_a) and (1L_b) transitions, and calculated to have $\sim 70\%$ and $\sim 50\%$ CT character, respectively.⁶ The position of

(1) National Science Foundation Trainee, 1965–1968.

(2) R. C. Hahn, P. H. Howard, S.-M. Kong, G. A. Lorenzo, and N. L. Miller, *J. Amer. Chem. Soc.*, **91**, 3558 (1969).

(3) Compound codings used here and henceforth (F5, S6, etc.) conveniently recall skeletal features: F stands for a fused cyclopropane ring, S for a spirocyclopropane; 5, 6, or 7 refers to the size of ring fused to the benzene ring.

(4) For a recent summary of pertinent literature, cf. B. R. Ree and J. C. Martin, *J. Amer. Chem. Soc.*, **92**, 1660 (1970), and references therein.

(5) For representations of delocalization in cyclopropylcarbonium ions, see P. von R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966).

(6) S. Nagakura, *Pure Appl. Chem.*, **7**, 79 (1963).

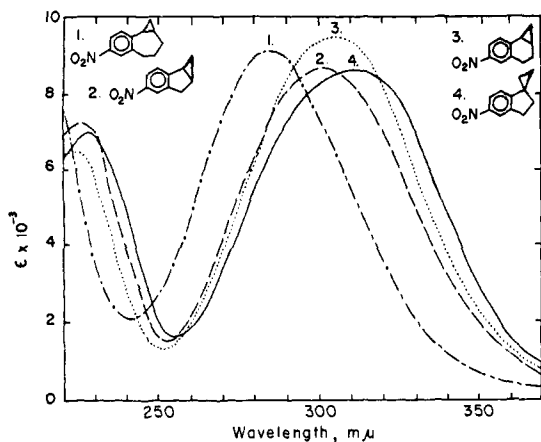


Figure 1. Ultraviolet spectra (95% EtOH) of β' -NO₂ F5, S5, F6, and F7.

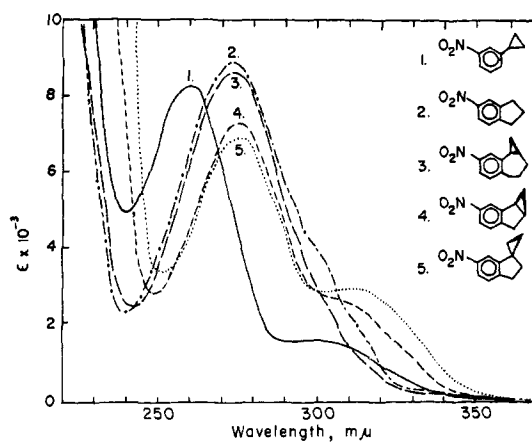


Figure 2. Ultraviolet spectra (cyclohexane) of β' -NO₂ F5, S5, F7, and reference compounds.

the 1L_b band is relatively little affected by an electron-donating substituent para to the nitro group, whereas the 1L_a band is more responsive to such substitution.^{7,8} Thus the single, broad-absorption band for each β' -nitro compound (Figure 1) may contain both the 1L_b and 1L_a transitions, with the 1L_b band buried under the more intense, more strongly shifted 1L_a band. When the cyclopropyl group is meta and an alkyl substituent is para to the nitro group as in the β -nitro derivatives (Figure 2), the 1L_a band appears at shorter wavelengths than for the β' -nitro compounds, reflecting the decreased electron-donating ability and/or polarizability of alkyl relative to cyclopropyl. If the β -nitro compounds are compared with *m*-nitrocyclopropylbenzene (no alkyl para to nitro), predictable¹² 12- to 15- $m\mu$ bathochromic shifts are noted for the 1L_a band (Figure 2), with smaller apparent bathochromic shifts for the 1L_b band.

The above analysis suggested the possibility that nitroarylcyclopropane systems having no substituent para to the nitro group in some cases might show enough separation between the 1L_a and 1L_b bands to allow assignment of more definite λ_{max} and ϵ_{max} values to the latter, and more clear relation of these properties to cyclopropane geometry. A study of the electronic spectra of α - and α' -NO₂-F5, S5, F6, S6, and F7 therefore was made. These series contain nitro and cyclopropyl groups ortho and meta to one another, respectively; it was of further particular interest to compare spectral properties in these two series with one another and with those in the β - and β' -nitro series, in view of the fact that cyclopropane geometry effects had appeared in both of the latter when classical resonance theory predicted such effects only for the β' -nitro systems.

Syntheses. The α -nitro derivatives of F5, S5, F6, S6, F7,^{13a} and corresponding reference compounds were ob-

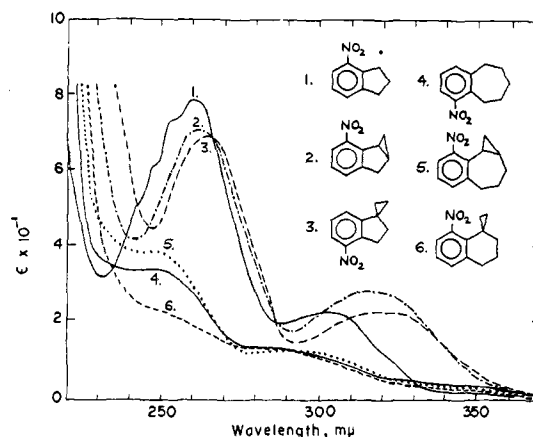


Figure 3. Ultraviolet spectra (hexane) of α -nitroindan, α -NO₂-F5, α' -NO₂-S5, α -nitrobenzosuberan, α -NO₂-F7, and α -NO₂-S6.

tained by nitration of the hydrocarbons and chromatographic separation from the product mixtures. Structure assignments for α -nitro compounds as well as α' -nitro isomers were made by a combination of nmr analysis and independent synthesis.^{13b}

The α' -nitro derivatives of F5, S5, F6, and S6 were prepared indirectly *via* the routes outlined in Scheme I.

Ultraviolet Spectra. Values of λ_{max} and ϵ_{max} for all α - and α' -nitro derivatives of F5, F6, F7, S5, and S6, α -nitroindan, α -nitrotetralin, α -nitrobenzosuberan, and *o*- and *m*-nitrocyclopropylbenzene in hexane or cyclohexane are assembled in Table I; selected spectra are shown in Figure 3.

Comparison of the data for α -nitro isomers of indan, tetralin, and benzosuberan indicates the presence of ring size effects; λ_{max} and ϵ_{max} decrease with increasing ring size for both the 1L_a and 1L_b transitions. No useful subdivision of these effects into (*e.g.*) ring strain effects and steric effects appears possible; wavelengths and intensities of α - and α' -nitrocyclopropyl derivatives therefore are best compared with those of the corresponding parent compounds.

(13) (a) The earlier inability to isolate α -NO₂-F7 from the nitration mixture² stemmed from the identical vpc retention times of the α - and α' -nitro isomers, and from the unusually slow rate of elution of the α -nitro isomer from a silica gel chromatography column ($\alpha' > \beta' > \beta > \alpha$). No precedent for this behavior was found in the present study or elsewhere. (b) Complete isomer distributions from nitration of F5, F6, F7, S5, and S6, a study of cyclopropane nmr anisotropy effects and mass spectral behavior in these systems will appear in separate papers.

(7) Cf. J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Wiley, New York, N. Y., 1963.

(8) The terms 1L_a and 1L_b , applied originally to electronic transitions in certain aromatic hydrocarbons,⁹ can be no more than notations of convenience here, since the excited states under consideration are products of extensive electron configuration interaction.^{10,11}

(9) J. R. Platt, *J. Chem. Phys.*, 17, 484 (1949).

(10) The electron configuration in the upper state is usually used to classify the transition.

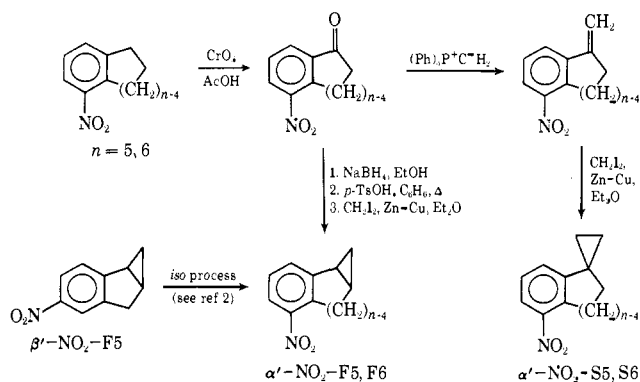
(11) Cf. H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press, New York, N. Y., 1967.

(12) Cf. H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962.

Table I. Values of $\lambda_{\max}^{\text{hexane}}$ ($m\mu$) and ϵ_{\max} for α - and α' -Nitro Derivatives and Reference Compounds

Compound	θ , deg	1L_a band			1L_b band		
		λ_{\max} , nm	Log ϵ	$\Delta\lambda$, nm	λ_{\max} , nm	Log ϵ	$\Delta\lambda$, nm
<i>m</i> -Nitrocyclopropylbenzene		260	3.91		301	3.19	
<i>o</i> -Nitrocyclopropylbenzene		250	3.65		295	3.21	
α -Nitroindan		259	3.89		301	3.37	
α' -NO ₂ -F5	25	265	3.79	6	311	3.31	10
α' -NO ₂ -S5	0	265	3.84	6	320	3.36	19
α -NO ₂ -F5	25	263	3.85	4	317	3.46	16
α -NO ₂ -S5	0	261	3.40	2	315	3.16	14
α -Nitrotetralin		257	3.64		~295	3.20	
α' -NO ₂ -F6	10	259	3.55	2	306	3.13	11
α' -NO ₂ -S6	10	262	3.53	5	~306	3.16	11
α -NO ₂ -F6	10	259	3.57	2	308	3.25	13
α -NO ₂ -S6	10	~250	3.35	-7	~285	3.10	-10
α -Nitrobenzo-suberan		249	3.54		~290	3.10	
α' -NO ₂ -F7	90	253	3.58	4	~294	3.10	4
α -NO ₂ -F7	90	249	3.59	0	294	3.14	4

The weaker, longer wavelength 1L_b band indeed is more clearly separated from the 1L_a band in these spectra than in the spectra of the β -nitro derivatives, enabling 1L_b λ_{\max} and ϵ_{\max} determinations to be made for most compounds. The improved band separation can

Scheme I

be seen to be primarily a result of a hypsochromic shift of the 1L_a band, as discussed previously.⁷ For all of the cyclopropyl systems derived from indan or tetralin except α -NO₂-S6, both the 1L_a and 1L_b bands are bathochromically shifted relative to α -nitroindan or tetralin, the 1L_a band by 2–6 $m\mu$, the 1L_b band by 10–19 $m\mu$. The 1L_b transition thus is more sensitive to the presence of the cyclopropyl group, although the data do not permit any cyclopropane geometry correlation in this range ($\theta = 0$ –25°). In contrast, both bands for α - and α' -NO₂-F7 are bathochromically shifted by not more than 4 $m\mu$, relative to the corresponding bands for α -nitrobenzoesuberan. For the 1L_b transition this shift is significantly smaller than those seen for the indan and tetralin derivatives. This behavior is taken as a reflection of the very poor cyclopropane geometry for conjugative interaction in the F7 system, and as further evidence for the importance of cyclopropane geometry in the electronic spectra of nitrophenylcyclopropanes.

Pronounced hypsochromic shifts and reduced intensities appear for both bands of α -NO₂-S6 and the 1L_a band of nitrocyclopropylbenzene (relative to α -nitrotetralin and *m*-nitrocyclopropylbenzene, respectively). These effects indicate severe steric interaction between the nitro and cyclopropyl groups, probably forcing both

moieties away from preferred conjugation geometries. However, ϵ_{\max} values, molecular models, nmr data,^{13b} and mass spectral peculiarities^{13b} indicate that the nitro group in α -NO₂-S5 also is severely twisted, yet the λ_{\max} values for this compound remain little affected.

Two striking features emerge from comparison of the spectra in Figures 1, 2, and 3. First, in molecules with good cyclopropane geometry for conjugation, the spectral features of *o*(α)-nitrocyclopropyl isomers resemble those of *m*(β and α')-nitro isomers more than those of *p*(β')-nitro isomers. This behavior, which could not be predicted from consideration of ground state resonance structures, is not novel, however. The uv spectra of *o*- and *m*-nitroanisoles, -nitrophenols, and -cyanophenols are all more similar to one another than to the para isomers.¹⁴ These compounds are all benzene derivatives containing one good electron donor and one good acceptor; the present nitrocyclopropyl systems clearly are similar in this respect.

Second, the *m*(β and α')-nitro isomers have lower energy (1L_b) transitions than do the para(β') isomers, again in contradiction to the predictions of ground-state resonance theory. Inability to explain excited state phenomena through application of classical resonance theory has been reported previously by (*e.g.*) Havinga¹⁵ and Zimmerman.¹⁶ These authors performed molecular orbital calculations indicating that in the first excited state of "donor-acceptor" disubstituted benzenes, electron transmission between such groups ortho or meta to each other is more facile than if the groups are para. Grinter and Heilbronner¹⁴ applied similar theoretical interpretations to the spectra of their donor-acceptor systems. Their calculation of the energy of a "typical" donor-acceptor charge-transfer excitation assumed a donor ionization potential of 10 eV; the ionization potential of cyclopropane itself has been reported to be as low as 9.96 eV,¹⁷ and would be expected to be lowered further by alkyl substitution, so that by this criterion

(14) R. Grinter and E. Heilbronner, *Helv. Chim. Acta*, **45**, 2496 (1962).

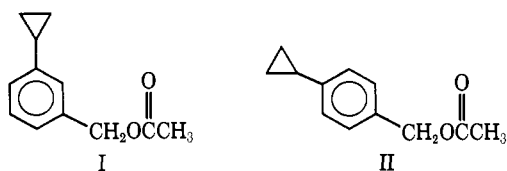
(15) E. Havinga, R. O. de Jongh, and M. E. Kronenberg, *ibid.*, **50**, 2550 (1967), and references therein.

(16) H. E. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc.*, **85**, 915 (1963); H. E. Zimmerman and S. Somasekhara, *ibid.*, **85**, 922 (1963).

(17) (a) D. W. Turner, *Advan. Phys. Org. Chem.*, **4**, 31 (1966); for other literature values, see (b) R. F. Pottle, A. G. Harrison, and F. P. Lossing, *J. Amer. Chem. Soc.*, **83**, 3204 (1961).

cyclopropyl is well qualified as a donor in a donor-acceptor system.¹⁸

Further direct evidence for the electron-donating ability of a *m*-cyclopropyl group in the first excited state has been provided recently by the facile photohydrolysis of *m*-cyclopropylbenzyl acetate (I); the para isomer (II) undergoes radical cyclopropyl ring opening under iden-



tical conditions.¹⁹ The uv spectral features observed in the present study are consistent with these photohydrolysis results, and with predictions based on molecular orbital theory encompassing first excited states. Thus in addition to reaffirming the importance of cyclopropane geometry requirements in electronic interaction with an adjacent π system, the present results demonstrate that such requirements can be manifested in an excited state of a system for which classical (ground state) resonance theory would not even predict conjugative interaction.

Experimental Section

Melting points and boiling points are uncorrected. Proton magnetic resonance spectra were obtained with a Varian A-60. Ultraviolet spectra were recorded on a Perkin-Elmer Model 202 in 1-cm matched fused-silica cells. Values of λ_{\max} were calibrated against holmium oxide glass; values of ϵ_{\max} were calculated from at least two different solute concentrations. Infrared spectra were taken on a Perkin-Elmer Infracord Model 137. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Scandinavian Microanalytical Laboratory, Herlev, Denmark.

2-Nitro-1,1a,6,6a-tetrahydrocycloprop[a]indene (α -NO₂-F5). Nitration of F5 and work-up as described previously² gave a crude product from which α -NO₂-F5 was isolated by silica gel chromatography (hexane elution). Recrystallization from hexane gave pale yellow crystals: mp 25–26°; ir (neat, NaCl) 1535, 1340, 811, 800, 745, and 679 cm⁻¹; nmr (CDCl₃) τ 2.08 (1 H, d, *J* = 8 cps, H ortho to NO₂), 2.58 (1 H, d, *J* = 8 cps, H para to NO₂), 2.83 (1 H, t, H meta to NO₂), 6.73 (3 H, m, benzylic), 8.03 (1 H, m, cyclopropyl methine), 8.74 (1 H, m, cyclopropyl anti), 9.90 (1 H, m, cyclopropyl syn). *Anal.* Calcd for C₁₀H₉NO₂: C, 68.56, H, 5.18; N, 8.00. Found: C, 68.53; H, 5.05; N, 7.96.

Preparation of 5-Nitro-1,1a,6,6a-tetrahydrocycloprop[a]indene (α' -NO₂-F5) (Method A). 4-Amino-5-nitro-1,1a,6,6a-tetrahydrocycloprop[a]indene (β' -NH₂- α' -NO₂-F5). In the manner described previously,² 200 mg (0.86 mmole) of β' -AcNH- α' -NO₂-F5 was obtained: mp 126.5–128°; ir 3240, 1660, 1550, and 1350 cm⁻¹; nmr (CDCl₃) τ 0.52 (1 H, broad s, NH), 1.82 and 2.55 (1 H each, d's, *J* = 8 cps), 7.80 (3 H, s, CH₃), and other peaks similar to the spectrum of parent F5. The nitroamide was hydrolyzed in aqueous ethanolic potassium hydroxide at room temperature to yield 113 mg (69%) of red nitroamine, which after recrystallization from hexane had mp 91–92°; ir (KBr) 3470, 3330 and 1625 cm⁻¹ (NH₂), and 1515 and 1338 (NO₂); nmr (CDCl₃) τ 2.80 and 3.40 (1 H each, d's, *J* = 8 cps), 4.35 (2 H, broad s, NH₂).

5-Nitro-1,1a,6,6a-tetrahydrocycloprop[a]indene (α' -NO₂-F5). Aqueous sodium nitrite (1 ml; 50 mg, 5 mmoles) was added slowly to a solution of β' -NH₂- α' -NO₂-F5 (80 mg, 4 mmoles) in 4 ml of water and concd sulfuric acid (1.1 g, 11 mmoles) at 2°. After 1 hr, chilled 50% hypophosphorous acid (1.1 g, 8 mmoles) was added; the mixture was kept at 0° for 24 hr, and worked up. The products from three such deaminations were combined and twice chromatographed (silica gel, hexane), giving 64 mg of α' -NO₂-F5 as a pale yellow oil: ir (KBr) 1520, 1339, 835, 812, 797, 770, 738, and 708 cm⁻¹; nmr (CDCl₃) τ 2.12 (1 H, d, *J* =

8 cps, β' -H), 2.48 (1 H, d, *J* = 8 cps, α -H), 2.80 (1 H, t, β -H), 6.55 (2 H, broad d, benzyl), and other peaks similar to those of parent F5. *Anal.* Calcd for C₁₀H₉NO₂: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.52; H, 5.19; N, 8.08.

Method B. 4-Nitroindan-1-one. A suspension of 18 g (0.18 mole) of chromic anhydride in 300 ml of acetic acid was added over 0.5 hr to a solution of α -nitroindan (10.96 g)²⁰ in 250 ml of acetic acid maintained at 24–26° with vigorous stirring. The reaction was quenched after 2 hr, and worked up to give a green solid. This was chromatographed on silica gel, using 5% ether-hexane to elute α -nitroindan (1.226 g). Elution with 10% ether-hexane yielded 4-nitroindan-1-one (6.445 g, 54%): mp 101–103° (lit.²¹ 104–105°); ir (KBr) 1720, 1610, 1525, 1350, 1330, 1260, 1050, 800, 780, and 745 cm⁻¹; nmr (CDCl₃) τ 1.54 (1 H, dd, *J*'s = 1 and 8 cps, H ortho to NO₂), 1.94 (1 H, dd, *J*'s = 1 and 8 cps, H para to NO₂), 2.35 (1 H, t, meta to NO₂), 6.37 (2 H, m, benzyl), and 7.22 (2 H, m, CH₂ α to C=O).

7-Nitroindene. Reaction of sodium borohydride (1.5 g) with an ethanolic solution of 4-nitroindan-1-one (1.48 g, 8.36 mmoles) afforded ~100% of crude nitro alcohol, which was dehydrated directly *via* refluxing 1 hr with *p*-toluenesulfonic acid (1.5 g) in toluene (250 ml). Filtration of the mixture through a 1-in. layer of activated silica gel and removal of solvent left 1.17 g (7.26 mmoles, 87%) of pale yellow 7-nitroindene: mp 85.5–87.0°; ir (KBr) 1510, 1325, 947, 808, 742, and 690 cm⁻¹; nmr (CDCl₃) τ 1.98 (1 H, dd, *J*'s = 1.4, 7.7 cps, 6-H), 2.33 (1 H, dd, *J*'s = 1.4, 7.7 cps, 4-H), 2.60 (1 H, t, 5-H), 3.07 and 3.28 (1 H each, dt's, *J*'s = 5.7, 1.7 and 1.7 cps, vinyl H's), and 6.12 (2 H, broad t, 1-H's).

α' -NO₂-F5. Reaction of 7-nitroindene (1.08 g) with iodomethylzinc iodide (from 9.8 g of zinc dust) as described for synthesis of spiro(cyclopropane-1,1'-tetralin)² gave a dark oil which on repeated silica gel chromatography and a final distillation gave ca. 10 mg of pale yellow oil with spectral properties identical with those reported for α' -NO₂-F5 obtained *via* method A (see above).

5'-Nitrospiro(cyclopropane-1,1'-indan) (α -NO₂-S5). Nitration of S5 (5.66 g, 39.2 mmoles) and work-up as described previously² gave a dark oil. The first band eluted on hexane-silica gel chromatography of this material was recrystallized from hexane to give 220 mg of yellow α -NO₂-S5: mp 26–26.5°; ir (neat, NaCl) 1520, 1350, 868, 820, 798, and 739 cm⁻¹; nmr (CDCl₃) τ 2.83 (3 H, broad m, aromatic), 7.13 (2 H, t, benzyl), 8.09 (2 H, t, cyclopropylcarbinyl), 8.68 (2 H, m, syn cyclopropyl), and 9.28 (2 H, m, anti cyclopropyl). *Anal.* Calcd for C₁₁H₁₁NO₂: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.88; H, 5.97; N, 7.31.

Preparation of α' -NO₂-S5. 4-Nitro-1-methyleneindan. A Wittig reaction between triphenylphosphonium methylene (44 mmoles) and 4-nitroindan-1-one (39 mmoles) was conducted as described for synthesis of 1-methyleneindan.² Hexane-silica gel chromatography of the black crude product and recrystallization from hexane gave 900 mg (13%) of yellow 4-nitro-1-methyleneindan: mp 39–41°; ir (KBr) 1640, 1520, 1345, 880, 775, 750, and 725 cm⁻¹; nmr (CDCl₃) τ 2.14 (1 H, d, *J* = 8 cps, H ortho to NO₂), 2.42 (1 H, d, *J* = 8 cps, H para to NO₂), 2.80 (1 H, t, meta to NO₂), 4.52 (1 H, t, *J* = 2.5 cps, syn vinyl), 4.92 (1 H, t, anti vinyl), 6.79 and 7.30 (2 H each, m, benzyl and allyl CH₂, respectively).

4'-Nitrospiro(cyclopropane-1,1'-indan) (α' -NO₂-S5). Reaction of iodomethylzinc iodide (15 mmoles) and 4-nitro-1-methyleneindan (900 mg, 5 mmoles) was conducted as described above for α' -NO₂-F5. Silica gel-silver nitrate chromatography (hexane elution) of the crude product yielded 54 mg (5.6%) of α' -NO₂-S5 as a yellow oil: ir (neat, NaCl) 1525, 1455, 1350, 1340, 1325, 1285, 805, and 740 cm⁻¹; nmr (CDCl₃) τ 2.10 (1 H, d, *J* = 8 cps, H ortho to NO₂), 2.75 (1 H, t, H meta to NO₂), 3.14 (1 H, d, *J* = 8 cps, para to NO₂), 6.52 and 7.83 (2 H each, t's, *J* = 7.5 cps, benzyl and cyclopropylcarbinyl CH₂'s, respectively), and 9.02 (4 H, d, cyclopropyl). *Anal.* Calcd for C₁₁H₁₁NO₂: C, 69.82; H, 5.86. Found: C, 70.03; H, 6.32.

7-Nitro-1a,2,3,7b-tetrahydro-1H-cyclopropa[a]naphthalene (α -NO₂-F6). The crude α -NO₂-F6 isolated from nitration of F6² (5.76 g) was recrystallized from hexane to give 2.3 g of almost colorless crystals: mp 46.5–49.0°; nmr (CDCl₃) τ 8.8–9.2 (2 H, m, cyclopropyl CH₂), 7.3–8.6 (6 H, m, remaining nonaromatic H's), 2.40 (1 H, dd, β -H), 2.93 (1 H, t, β' -H), and 2.80 (1 H, d, α' -H); uv $\lambda_{\max}^{\text{EtOH}}$ 268 m μ , ϵ 3740; $\lambda_{\max}^{\text{hexane}}$ 260 m μ , ϵ 3680; ir (neat, NaCl) 1525, 1350, 900, 860, 810, 772, 748, and 740 cm⁻¹. *Anal.* Calcd for C₁₁H₁₁NO₂: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.94; H, 5.86; N, 7.44.

(18) For extended discussion of intramolecular charge-transfer interaction and numerous pertinent references, see M. Oki and K. Mutai, *Tetrahedron*, **26**, 1181 (1970).

(19) L. B. Jones, *Petrol. Res. Found. Annu. Rep.*, **14**, 163 (1969).

(20) J. Lindner and J. Bruhin, *Chem. Ber.*, **60**, 435 (1927).

(21) H. Hoyer, *J. Prakt. Chem.*, **139**, 94 (1934).

8'-Nitrospiro(cyclopropane-1,1-tetralin) (α -NO₂-S6). Crude α -NO₂-S6 from nitration of S6² on recrystallization from hexane afforded almost colorless crystals melting below room temperature: nmr (CDCl₃) τ 9.2 (4 H, s, cyclopropyl CH₂'s), 7.9–8.6 (4 H, m, 2' and 3' CH₂'s), 7.13 (2 H, t, benzyl), and 2.76 (3 H, sharp m, aromatic H's); uv $\lambda_{\max}^{\text{EtOH}}$ 259 m μ , ϵ 2220; ir (neat, NaCl) 1560, 1365, 821, 800, and 749 cm⁻¹. *Anal.* Calcd for C₁₂H₁₃NO₂: C, 70.91; H, 6.45; N, 6.89. Found: C, 71.02; H, 6.37; N, 6.69.

Preparation of α' -NO₂-F6. 5-Nitro-1-tetralone.²² Chromium trioxide (36 g, 360 mmoles) in 720 ml of acetic acid was added to a solution of 5-nitrotetralin²³ (36 g, 200 mmoles) in 720 ml of acetic acid. The solution was stirred for 2.5 hr and diluted with 300 ml of water, and the organic layer was extracted into chloroform. The chloroform layer was washed with saturated sodium bicarbonate and dried over magnesium sulfate. Removal of solvent and several recrystallizations from 95% ethanol yielded 13.3 g (35%) of 5-nitro-1-tetralone: mp 99–101° (lit.²² 102°); nmr (CDCl₃) τ 6.78 (2 H, t, α -carbonyl H's), 7.26 (2 H, t, benzyl), 7.5–8.1 (2 H, m, remaining nonaromatic H's), 2.50 (1 H, t, β -H), 1.92 (1 H, dd, β' -H), and 1.68 (1 H, dd, α -H); ir (KBr) 1675, 1600, 1520, 1340, 920, 898, 871, 852, 812, 788, 757, 732, and 720 cm⁻¹.

5-Nitrotetrahydronaphth-1-ol. 5-Nitro-1-tetralone (4.0 g, 21 mmoles) in 120 ml of 95% ethanol was reduced by sodium borohydride (3.47 g, 92 mmoles) to yield ~100% of 5-nitrotetrahydronaphth-1-ol as a yellow oil: nmr (CDCl₃) τ 5.1–5.4 (1 H, m, α to OH), 6.83 (1 H, s, hydroxyl H), 6.9–7.3 (2 H, m, benzyl CH₂), 7.9–8.2 (4 H, m, other CH₂'s), 2.55–2.85 (1 H, m, 7-H), 2.17–2.38 (2 H, m, 6-H and 8-H); ir (neat, NaCl) 3300, 1520, 1340, 985, 798, 761, 732, and 718 cm⁻¹.

8-Nitro-1,2-dihydronaphthalene. A solution of 5-nitrotetrahydronaphth-1-ol (4.4 g, 22.8 mmoles) and *p*-toluenesulfonic acid (1.0 g, 5.2 mmoles) in 100 ml of benzene was refluxed 1 hr with extraction of water. Work-up and crystallization from hexane yielded 3.45 g (87%) of 8-nitro-1,2-dihydronaphthalene: mp 31.0–31.5°; nmr (CDCl₂) τ 7.5–7.9 (2 H, m, allyl CH₂), 7.01 (2 H, t, benzyl CH₂), 3.53 (1 H, d, benzyl vinyl H), 3.92 (1 H, dt, other vinyl H), 2.65–2.90 (2 H, m, 5-H and 6-H), and 2.30–2.50 (1 H, m, 7-H); uv $\lambda_{\max}^{\text{EtOH}}$ 260 m μ , ϵ 12,600; $\lambda_{\max}^{\text{hexane}}$ 258 m μ , ϵ 13,500; ir (neat, NaCl) 1520, 1340, 862, 820, 800, 770, 756, 732, and 678 cm⁻¹. *Anal.* Calcd for C₁₀H₉NO₂: C, 68.56; H, 5.18; N, 8.00. Found: C, 69.03; H, 5.27; N, 8.05.

4-Nitro-1a,2,3,7b-tetrahydro-1H-cyclopropa[a]naphthalene (α' -NO₂-F6). Reaction of 8-nitro-1,2-dihydronaphthalene (2.0 g, 11.4 mmoles) with iodomethylzinc iodide (100 mmoles) and work-up as for synthesis of α' -NO₂-S5 yielded 0.2 g (9%) of α' -NO₂-F6 as a

yellow oil; nmr (CDCl₃) τ 2.45 (1 H, dd, β' -H), 2.54 (1 H, dd, α -H), 2.84 (1 H, t, β -H), nonaromatic absorptions similar to those of parent F6;² uv $\lambda_{\max}^{\text{EtOH}}$ 270 m μ , ϵ 3180; $\lambda_{\max}^{\text{hexane}}$ 259 m μ , ϵ 3540; ir (neat, NaCl) 1520, 1340, 856, 838, 807, 795, 768, 749, and 730 cm⁻¹. *Anal.* Calcd for C₁₁H₁₁NO₂: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.61; H, 5.91; N, 7.35.

Preparation of α' -NO₂-S6. 5-Nitro-1-methylenetetralin. A Wittig reaction between triphenylphosphonium methylide (74 mmoles) and 5-nitro-1-tetralone (9.0 g, 47 mmoles) was conducted and worked up as described for 4-nitro-1-methyleneindan to yield 3.15 g (35%) of 5-nitro-1-methylenetetralin: mp 31.5–32.5°; nmr (CDCl₃) τ 2.25 (1 H, dd, 8-H), 2.42 (1 H, dd, 6-H), 2.88 (1 H, t, 7-H), nonaromatic absorptions similar to those of parent 1-methylenetetralin;² uv $\lambda_{\max}^{\text{EtOH}}$ 248 m μ , ϵ 14,800; $\lambda_{\max}^{\text{hexane}}$ 245 m μ , ϵ 18,750; ir (neat, NaCl) 1520, 1350, 897, 816, 802, 746, and 722 cm⁻¹. *Anal.* Calcd for C₁₁H₁₁NO₂: C, 69.82; H, 5.86; N, 7.40. Found: C, 70.01; H, 6.08; N, 7.37.

5-Nitrospiro(cyclopropane-1,1'-tetralin) (α' -NO₂-S6). Reaction of 5-nitro-1-methylenetetralin (2.0 g, 10.5 mmoles) with iodomethylzinc iodide (100 mmoles) and work-up as in synthesis of α' -NO₂-S5 yielded 0.49 g (23%) of α' -NO₂-S6: mp 82.0–83.0°; nmr (CDCl₃) τ 2.49 (1 H, dd, β' -H), 2.83 (1 H, t, β -H), 3.17 (1 H, dd, α -H; compare 8-H of precursor), and nonaromatic absorptions similar to those of parent S6;² uv $\lambda_{\max}^{\text{EtOH}}$ 271 m μ , ϵ 3050; $\lambda_{\max}^{\text{hexane}}$ 262 m μ , ϵ 3360; ir (KBr) 1520, 1350, 898, 818, 803, 772, 747, 723, and 712 cm⁻¹. *Anal.* Calcd for C₁₂H₁₃NO₂: C, 70.91; H, 6.45; N, 6.89. Found: C, 71.05; H, 6.63; N, 6.77.

α -Nitrobenzosuberane. Crude α -nitrobenzosuberane² was rechromatographed (silica gel-hexane) with exclusion of light. Recrystallization (hexane) of the eluate afforded pale yellow crystals: mp 48–49.5°; nmr (CDCl₃) τ 2.55 (1 H, dd, H ortho to NO₂), 2.68 (1 H, dd, H para to NO₂), 2.89 (1 H, t, meta to NO₂), 7.14 (4 H, m, benzyl CH₂'s), and 8.30 (6 H, m, other CH₂'s); ir (KBr) 1525, 1358, 956, 854, 837, 800, 781, 754, 740, and 726 cm⁻¹. *Anal.* Calcd for C₁₁H₁₃NO₂: C, 69.09; H, 6.85; N, 7.33. Found: C, 68.98; H, 6.73; N, 7.23.

8-Nitro-1,1a,2,3,4,8b-hexahydrobenzo[a]cyclopropa[c]cycloheptane (α' -NO₂-F7). The chromatography column used to separate α' -, β' -, and β -nitro isomers from nitration of F7² was flushed with benzene. Solvent removal, silica gel-hexane chromatography of the residue, and recrystallization from hexane gave α -NO₂-F7 as pale yellow crystals: mp 67–67.5°; nmr (CDCl₃) τ 2.40 (1 H, overlapping d's, β -H), 2.71 (2 H, m, β' - and α' -H's), 6.58 (1 H, uneven sextet, benzyl H), 7.36 (1 H, quartet further split, benzyl H), 7.6–8.7 (4 H, m, CH₂CH₂), 8.7–9.1 (2 H, m, cyclopropyl methine), and 9.5–10.1 (2 H, m, cyclopropyl CH₂); ir (CHCl₃) 1520, 1350, 838, and 811 cm⁻¹. *Anal.* Calcd for C₁₂H₁₃NO₂: C, 70.91; H, 6.45; N, 6.89. Found: C, 70.80; H, 6.49; N, 6.84.

(22) J. D. Riedel, *Chem. Zentralbl.*, **95** (II), 1405 (1924).

(23) G. Schroeter, *Justus Liebig's Ann. Chem.*, **426**, 39 (1922).