homogeneous, and the volume of the solution was reduced to *ca.* 45 ml. When cooled to 0°, the mixture deposited dark brown needles, mp 186–189° (sealed tube). *Anal.* Calcd for $C_{24}H_{20}N_4$: C, 79.09; H, 5.53. Found: C, 78.86; H, 5.33.

Determination of Equilibrium Constants. The Benesi–Hildebrand treatment was used to determine the molar extinction coefficients and equilibrium constants. In a typical determination four concentrations were prepared, with the mole fraction of the donor varying from about 0.010 to about 0.033, while the concentration of the TCNE was held between 0.007 and 0.011 *M*. Good straight lines were obtained using the four points for each complex except for [3.3]- and [9]paracyclophane–TCNE salts whose *K*'s were determined only from least-squares analyses. The recorded values of the *K*'s for the other complexes were calculated both by least-squares analyses and Benesi–Hildebrand plots, and the values from each were in good agreement.

Cyclopropyl Aromatic Chemistry. I. Ultraviolet Spectra of Certain Cyclopropyl Aromatic Systems

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Abstract: The ultraviolet spectra of α- and β-cyclopropylnaphthalenes (I and II) resemble those of the corresponding methylnaphthalenes much more closely than those of α- and β-alkenylnaphthalenes. Data are tabulated to support the suggestion that a minimal electron-attracting ability of the naphthalene π system evokes a minimal conjugative response from the cyclopropyl group. To answer the question of the dependence of cyclopropane conjugation on geometry in arylcyclopropanes, uv spectra were obtained of 3- and 4-nitro-1,1a,6,6a-tetrahydrocycloprop-[*a*]indenes (β- and β'-NO$_2$-IV), 6'- and 5'-nitrospiro[cyclopropane-1,1'-indans] (β- and β'-NO$_2$-V), 5-nitro-1a,2,3,7b-tetrahydro-1H-cyclopropa[*a*]naphthalene (β'-NO$_2$-VI), 6'-nitrospiro[cyclopropane-1,1'-tetralin] (β'-NO$_2$-VII), and 7- and 6-nitro-1,1a,2,3,4,8b-hexahydrobenzo[*a*]cyclopropa[*c*]cycloheptenes (β- and β'-NO$_2$-VIII). Values for λ_{max}'s (^1L_a band, 95% EtOH) are: β-nitroindan, 282 mμ; β-NO$_2$-IV and β-NO$_2$-V, 282; β-NO$_2$-VIII, 280 (nitro *meta* to cyclopropyl in β series); β'-NO$_2$-VIII, 285; β'-NO$_2$-IV, 301; β'-NO$_2$-VI and β'-NO$_2$-VII, 306; β'-NO$_2$-V, 313 (nitro *para* to cyclopropyl in β' series). The absence of noticeable differences in the maxima of β-nitroindan, β-NO$_2$-IV, and β-NO$_2$-V is attributed to an absence of inductive donation by the cyclopropyl group to the nitroaromatic chromophore. The bathochromic λ_{max} shifts from β-NO$_2$-IV to β'-NO$_2$-IV and from β-NO$_2$-V to β'-NO$_2$-V are seen as results of cyclopropane conjugative interaction which is possible only in the β'-nitro systems. The bathochromic λ_{max} shifts in the β' series from β'-NO$_2$-VIII to β'-NO$_2$-V are related to increasingly favorable cyclopropane geometries for conjugation. It is concluded that cyclopropane conjugation in cyclopropyl aromatic systems is a spectroscopically detectable function of cyclopropane geometry if the interacting chromophore is sufficiently electron attracting.

It is widely accepted that the functioning of a cyclopropane ring as a ground-state electron donor, as in conjugation with neighboring unsaturated systems,[2,3] in neighboring group interaction with carbonium ions,[4] and in interaction with various electrophilic reagents,[5] involves specific steric requirements for maximum effect. Increasingly, attention has been directed also to the effects of cyclopropyl substitution on the electronic spectra of π-electron systems.[6–10] Results of

most of these studies indicate that cyclopropane geometry has an important effect on electronic spectral characteristics. However, for vinylcyclopropanes[9] and arylcyclopropanes,[11] geometric factors have been reported to be unimportant.

In an attempt to begin to accommodate this apparent divergence in the spectral behavior of cyclopropyl-substituted π systems, we have carried out a study of the ultraviolet spectra of a series of cyclopropyl aromatic compounds. The data presented here allow further evaluation of resonance and induction factors, and of conformation effects in cyclopropyl aromatic systems. We also discuss the role of chromophore electronegativity in affecting the auxochromic character of cyclopropanes.

Results and Discussion

Differences in ultraviolet absorption characteristics of certain α- and β-alkenylnaphthalenes have been attributed to steric interaction of α substituents with the naphthalene *peri* hydrogen, which can force the

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(2) H. C. Brown and J. C. Cleveland, *J. Am. Chem. Soc.*, **88**, 2051 (1966).

(3) T. Sharpe and J. C. Martin, *ibid.*, **88**, 1817 (1966).

(4) H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **89**, 1953 (1967); M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967).

(5) L. Joris, P. von R. Schleyer, and R. Gleiter, *ibid.*, **90**, 327 (1968), and references therein.

(6) For a review, see J.-P. Pete, *Bull. Soc. Chim. France*, 357 (1967).

(7) W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.*, **89**, 3449 (1967).

(8) R. E. Pincock and J. Haywood-Farmer, *Tetrahedron Letters*, 4759 (1967).

(9) C. H. Heathcock and S. R. Poulter, *J. Am. Chem. Soc.*, **90**, 3766 (1968), and references therein.

(10) M. J. Jorgenson and T. Leung, *ibid.*, **90**, 3769 (1968), and references therein.

(11) A. L. Goodman and R. H. Eastman, *ibid.*, **86**, 908 (1964).

α-alkenyl group away from the coplanar conformation needed for maximum conjugative interaction.[12] These phenomena prompted us to look for similar effects in α- and β-cyclopropylnaphthalenes (I and II), syntheses of which are outlined in Chart I.

Chart I.
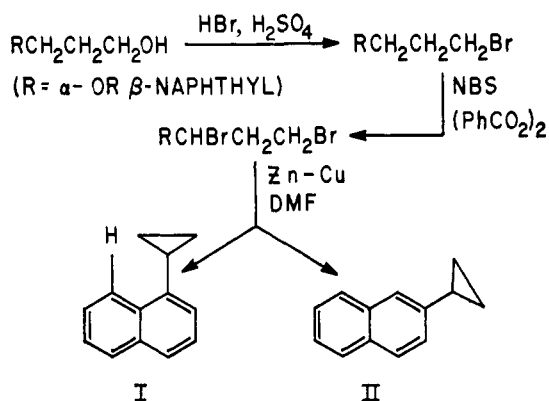
Models indicate that the α-cyclopropyl group does not have free rotation around its bond to the naphthalene carbon, because of interaction with the *peri* hydrogen. Preferred conformations of I thus may have

A (θ = 0°)
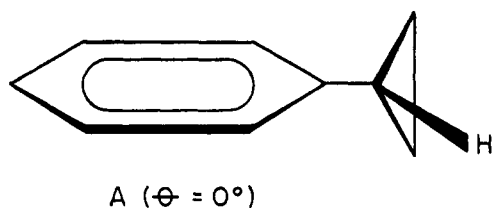
the cyclopropane ring swiveled away from the bisected geometry normally considered to be needed for maximum electronic interaction with an adjacent π system.[2,3] This geometry is exemplified in structure A, in which θ is defined as the angle made by the cyclopropyl methine carbon–hydrogen bond with the plane of the benzene ring.[11] The cyclopropane ring is thus perpendicular to the plane of the aromatic system in this conformation. To the extent that such electronic interaction occurs, and if there is a geometry requirement for cyclopropyl conjugation with the naphthalene π system, one might expect to see effects of steric hindrance in the electronic spectra of I and II.

Selected data from the uv spectra of some naphthalene derivatives are assembled in Table I. The α- and β-methylnaphthalenes have been chosen as comparison standards. We will consider the β system first. The listed λ_{max} values for β-isopropenylnaphthalene and β-(1-cyclohexenyl)naphthalene show substantial bathochromic shifts for both bands, compared to the corresponding values for β-methylnaphthalene. It has been suggested[12] that even in the β-cyclohexenyl system, with the largest of the substituents included here, there is minimal hindrance to achievement of the coplanarity needed for maximum orbital overlap of the vinyl π system and the naphthalene π system. The λ_{max} values for β-cyclopropylnaphthalene (II) are most similar to those for β-methylnaphthalene. Since steric hindrance is negligible in the β position, and the electron-attracting ability of naphthalene is greater here than at the

(12) L. H. Klemm, H. Ziffer, J. W. Sprague, and W. Hodes, *J. Org. Chem.*, **20**, 190 (1955).

Table I. Uv Absorption Maxima for Some Substituted Naphthalenes

Naphthalene substituent	λ_{max}, mμ (log ϵ_{max})	
	${}^1B_b$ band	${}^1L_a$ band
β-Methyl[a,b]	224 (4.94)	275 (3.68)
β-Cyclopropyl[a,c]	227.5 (4.90)	277 (3.72)
β-Isopropenyl[a,d]	238 (4.70)	283 (4.05)
β-(1-Cyclohexenyl)[e,f]	247 (4.61)	286 (4.08)
α-Methyl[a,c]	224 (4.99)	282 (3.69)
α-Cyclopropyl[a,c]	224.5 (4.86)	283 (3.82)
α-Propenyl[a,g]	228 (4.73)	296 (3.97)
α-(1-Cyclohexenyl)[e,f]	225–6 (4.93)	282 (4.07)

[a] 95% EtOH. [b] Data from R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1951. [c] This work. [d] Data from J. Jacques, M. Legrand, and J. Bourdon, *Bull. Soc. Chim. France*, 362 (1954). [e] Cyclohexane. [f] Data from ref 12. [g] Data from R. N. Beale and E. M. F. Roe, *J. Chem. Soc.*, 2888 (1951).

α position,[13] any exercise of the electron-donating capacity of the cyclopropane ring should be evident here. However, there is only a very minimal bathochromic shift for II, relative to β-methylnaphthalene. It is concluded that the naphthalene system, particularly in the excited electronic states involved here, does not have sufficient electron-attracting power to make any great demand on the conjugative ability of the β-cyclopropyl group. What little conjugative electron donation is provided by the cyclopropane endocyclic orbital(s) appears to be approximately counterbalanced by the inductive electronegativity of the cyclopropane exocyclic orbital relative to that of an ordinary alkyl group (e.g., methyl).[14]

Of the α systems in Table I, only the α-propenylnaphthalene maxima are bathochromically shifted, relative to those of α-methylnaphthalene. The lack of conjugative effect in α-(1-cyclohexenyl)naphthalene has been attributed to steric interaction of the cyclohexene ring and the naphthalene *peri* hydrogen.[12] Steric hindrance is also present in I, as discussed previously. The low-field *peri*-proton absorption in the nmr spectrum of I (see Experimental Section) may be consistent with preferred conformations in which the cyclopropane ring does not achieve bisected geometry.[15] The uv spectrum of I shows absorption maxima very similar to those of α-methylnaphthalene. Again, this similarity may be ascribed to a balance of conjugative and inductive effects of the cyclopropane ring, made possible by the minimal electron demand of the naphthalene ring. However, this rationalization, to the extent that it admits any significant conjugative effect, now requires either that the steric effect of the naphthalene *peri* hydrogen is minimal in preventing achievement of optimum cyclopropane geometry, or that the cyclopropane ring has no geometric requirements for conjugative interaction. If conjugative interaction is minimal, no conclusions can be drawn concerning the importance of cyclopropane geometry.

While the above work was in progress, Goodman and Eastman[11] reported that the ultraviolet absorption spectra of 1,1a,6,6a-tetrahydrocycloprop[a]indene (IV),

(13) Y. Okamoto and H. C. Brown, *J. Am. Chem. Soc.*, **79**, 1903 (1957).

(14) For a summary of theories of bonding of cyclopropanes see W. A. Bernett, *J. Chem. Educ.*, **44**, 17 (1967), and references therein.

(15) (a) K. Tori and K. Kitahonoki, *J. Am. Chem. Soc.*, **87**, 386 (1965), and references therein; (b) V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966), and references therein.

spiro[cyclopropane-1,1'-indan] (V), and 1a,2,3,7b-tetra-hydro-1H-cyclopropa[a]naphthalene (VI) are almost superimposable, despite the different geometries of the cyclopropane rings in these compounds. They concluded that there is no preferred geometry for conjugation of a cyclopropane ring with a benzene ring.
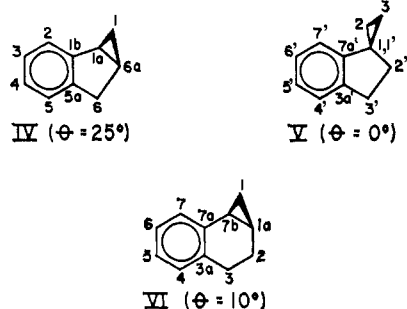
It occurred to us that the concept of minimal cyclopropane conjugation in the presence of minimal electron demand might apply to rationalization of the spectral features noted for IV, V, and VI. This concept has the additional appeal of not conflicting with the mass of evidence attesting to the importance of geometry in systems where cyclopropane participation is more strongly evoked.[2-11]

A survey of spectroscopic data in the literature provides evidence pertaining to the magnitude of cyclopropane substituent effects on the uv spectra of π systems of varying electronegativity. In Table II, reported λ_{max} values for some substituted uv chromophores are listed in rough order of increasing electron-attracting ability; for each chromophore the effects of alkyl, cyclopropyl, and alkenyl substitution are given where available.

Table II. Substituent Effects on Ultraviolet Absorption Maxima

| Compound	λ_{max}, mμ	$\Delta\lambda_{max}$, rel to alkyl group	Ref
Indan and 1,1'-dimethylindan	~218[a]		11
IV and V	~225[a]	~7	11
Indene and 1-methyleneindan	~250[a]	~32	11
Tetralin	~218[a]		11
VI	~225[a]	~7	11
1,2-Dihydronaphthalene	~260[a]	~42	11
Ethylbenzene	206[a]		d
Cyclopropylbenzene (III)	220[a]	14	d
Styrene	245.5[a]	39.5	d
Isopropyl methyl ketone (XX)	193[a]		d
Cyclopropyl methyl ketone (YY)	208[a]	15	d
Methyl vinyl ketone (ZZ)	219[a]	26	d
p-Nitroethylbenzene	274.5[a]		e
p-NO₂-III	297[a]	22.5	
p-Nitrostyrene	300[b]	25.5	f
2,4-Dinitrophenylhydrazone (DNPH) of XX	368[c]		g
2,4-DNPH of YY	375[c]	7	g
2,4-DNPH of ZZ	374[c]	6	g

[a] In 95% ethanol. [b] In methanol. [c] In methylene chloride. [d] M. T. Rogers, *J. Am. Chem. Soc.*, **69**, 2544 (1947). [e] W. M. Schubert, J. Robins, and J. L. Haun, *ibid.*, **79**, 910 (1957). [f] J. R. Joy and M. Orchin, *ibid.*, **81**, 305 (1959). [g] M. F. Hawthorne, *J. Org. Chem.*, **21**, 1523 (1956).

It can be noted from Table II that the cyclopropyl group in all cases causes a greater bathochromic shift than does an alkyl group, and that the magnitude of

the shift approaches that of an alkenyl group as the electronegativity of the chromophore increases. A conclusion similar to that previously reached[16] is that the cyclopropyl group makes a conjugative electron contribution commensurate with the demands of the chromophore. Except for the present reported naphthalene systems (Table I), compounds IV–VI in Table II show the smallest bathochromic shifts for cyclopropyl substitution, and therefore appear to be relatively insensitive models for detecting geometry effects on cyclopropane conjugation.

The broadness of the ^1L_a band maxima prevents confident assignments of λ_{max} values for indan, tetralin, and cyclopropane derivatives IV–VI (Table II). However, it was reported[11] that for the relatively sharp ^1L_b band maxima near 270 mμ, there are small λ_{max} and ϵ_{max} increases in the order VI < IV < V. These changes were attributed to increasing ground-state strain perturbations in the same order. We have confirmed these results, but noticed that for indan and tetralin ^1L_b transitions (0–0 band), λ_{max} and ϵ_{max} changes go in opposite directions. Comparison of, e.g., indan and IV, or tetralin and VI is similarly inconsistent. Strain factors alone therefore cannot provide a common rationale for both energy and intensity changes in these systems. An earlier study[17] of ^1L_b 0–0 band characteristics of the benzocycloalkene series benzocyclobutene through benzocyclooctene showed no simple relation between λ_{max} and ϵ_{max} changes.

To gain further insight into the roles of cyclopropane geometries and strain perturbations in the uv spectra of cyclopropyl aromatic systems, it was decided to prepare spiro[cyclopropane-1,1'-tetralin] (VII) and 1,1a,-2,3,4,8b-hexahydrobenzo[a]cyclopropa[c]cycloheptene (VIII). System VIII is of particular interest because the value of θ as estimated from the most stable conformation based on consideration of molecular models[18] is very close to 90°. This angle corresponds to a
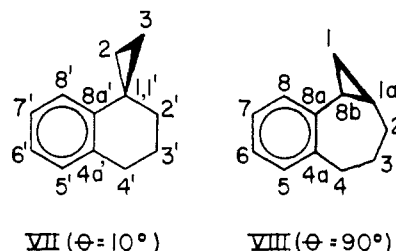
geometry which normally totally precludes conjugative interaction of the cyclopropane ring with an adjacent π system.

The ^1L_b 0–0 band λ_{max} and ϵ_{max} values for IV–VIII, the corresponding benzocycloalkenes, and other benzene hydrocarbon derivatives of interest are listed in Table III.

Inspection of Table III leads to the conclusion that absorption intensities may indeed increase with increasing ground-state strain. However, such strain appears to be produced in a variety of sometimes subtle ways, and while intensity variations in series of closely

(16) R. Fuchs, C. A. Kaplan, J. J. Bloomfield, and L. F. Hatch, *J. Org. Chem.*, **27**, 733 (1962).
(17) W. R. Moore, E. Marcus, S. E. Fenton, and R. T. Arnold, *Tetrahedron*, **5**, 179 (1959).
(18) Preferred conformations of IV, V, and VI are similarly based.[11]

Table III. Ultraviolet Absorption λ_{max} and ϵ_{max} Values (^1L_b Transition, 0–0 Band) for Some Benzene Derivatives

Compound	λ_{max}, mμ	ϵ_{max}	$\Delta\lambda$
Isopropylbenzene[a]	268	140	
Cyclopropylbenzene[a]	275	380	7
Styrene[a]	291	600	23
o-Diethylbenzene[b]	271	200, 208	
Benzocyclopropene[c]	275	1900	
Benzocyclobutene[d]	271.5	1860	
Indan[e]	273 (273)[f]	1390 (1410)[f]	
IV[e]	278	1300	5
V[e]	281	1790	8
Benzonorbornene[g]	271	1120	
Benzonorbornadiene[h]	276	500	
Tetralin[e]	274 (274)[f]	623 (631)[f]	
VI[e]	277	427	3
VII[e]	279	917	5
1,4-Dihydronaphthalene[i]	274	850	
Benzosuberan[e]	271 (271)[j]	269 (277)[j]	
VIII[e]	272	307	1

[a] Cyclohexane; data from ref 19c. [b] Isooctane; *API Research Project*, **44**, II (1951). [c] Cyclohexane; E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Letters*, 3625 (1965). [d] Ethanol; M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.*, **80**, 2255 (1958). [e] Hexane; this work. [f] Isooctane; data from ref 19a. [g] n-Heptane; data from ref 19a. [h] Cyclohexane; G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958). [i] Hexane; R. A. Morton and A. J. A. de Gouveia, *J. Chem. Soc.*, 916 (1934). [j] Isooctane; ref 17.

the same λ_{max}, have ϵ_{max}'s at the lower, middle, and upper levels of the intensity range covered in Table III. The reported[11] bathochromic effect of introducing a cyclopropane ring into a benzocycloalkene system is confirmed and extended, and though the $\Delta\lambda$ values are small, appears to be fairly well correlated with cyclopropane geometry in these compounds. However, it was felt that more responsive systems were needed to answer more unequivocally the question of geometry effects on conjugation in cyclopropyl aromatics.

The powerful influence of nitro substitution on electronic spectra (previous observations[20] and data in Table II) suggested that such structures could be prepared simply by introduction of a nitro group *para* to the cyclopropyl group in IV–VIII. As strain-free reference compounds, *m*- and *p*-nitrocyclopropylbenzene (*m*- and *p*-NO$_2$-III) were used. To help evaluate effects of ring size on spectral characteristics, β-nitroindan, β-nitrotetralin, and β-nitrobenzosuberan were employed. To determine the importance of relative positions of the nitro and cyclopropyl group, β-NO$_2$-IV, β-NO$_2$-V, and β-NO$_2$-VIII (nitro *meta* to cyclopropyl) were prepared. Syntheses of previously unknown compounds are outlined in Chart II. The classical sequence for converting, *e.g.*, a *p*-nitro com-

Chart II. Syntheses of III – VIII and Nitro Derivatives
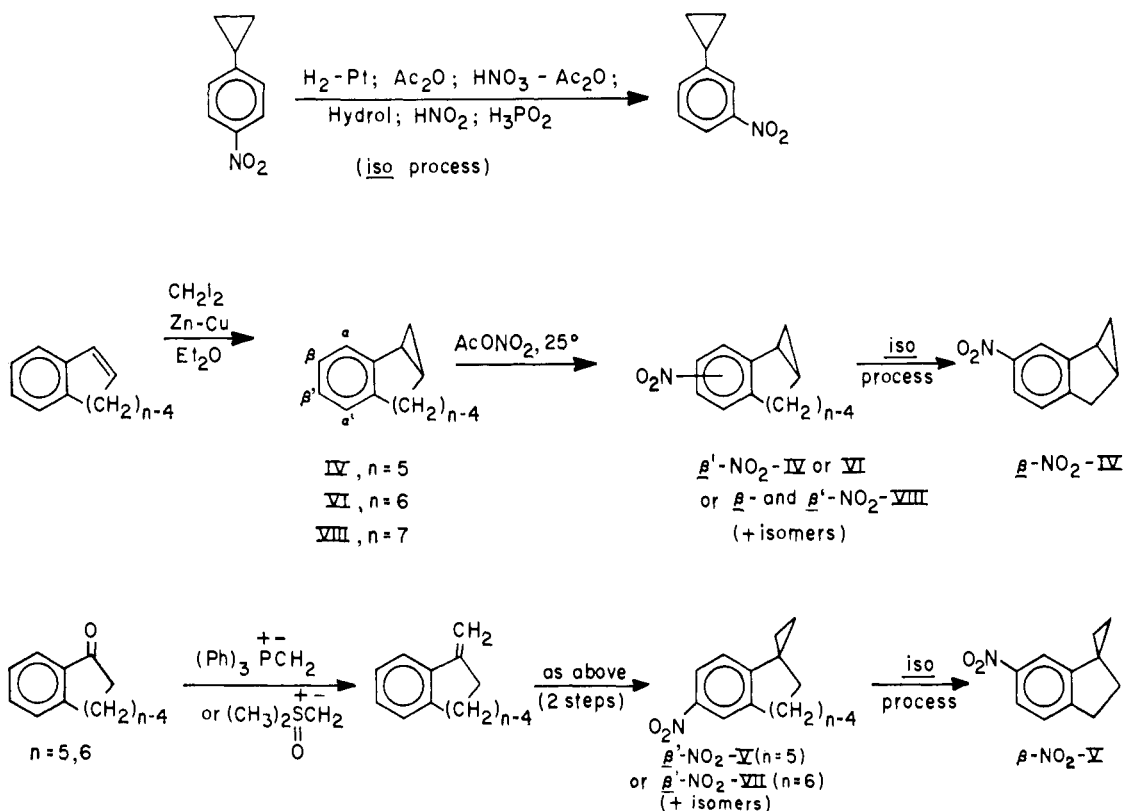
related structures may be rationalizable[17,19] no single unifying concept is apparent.

Absorption maxima clearly are not governed by the same structural features affecting intensities. For example, the three compounds o-diethylbenzene, benzocyclobutene, and benzonorbornene, with essentially

pound to a *m*-nitro compound has been termed the "iso process" for brevity.

Nitrations

Under the conditions given in Chart II, nitration of hydrocarbons IV–VII afforded the β'-nitro isomer (nitro *para* to cyclopropyl) as the major product. It

(19) (a) H. Tanida and R. Muneyuki, *J. Am. Chem. Soc.*, **87**, 4794 (1965); (b) M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962; (c) W. W. Robertson, J. F. Music, and F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5260 (1950).

(20) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962.
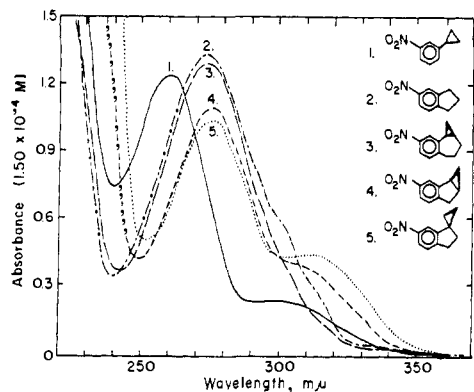
Figure 1. Ultraviolet spectra (cyclohexane) of β-nitro derivatives of III, IV, V, VIII, and indan.

was expected from consideration of σ^+ values for *freely rotating* p-cyclopropyl and p-ethyl (-0.46 and -0.29, respectively) and from estimation of the preferred cyclopropane conformations in IV–VII that the cyclopropyl group would dominate directive effects in these systems.[21] In contrast, nitration of hydrocarbon VIII gave more β- than β'-nitro isomer, and considerable amounts of α'-nitro isomer, while no α-nitro isomer was isolated. This result constitutes the second reported example of electrophilic attack on a cyclopropyl aromatic hydrocarbon occurring predominantly *meta* to the cyclopropyl group; Brown and Cleveland[2] noted that acetylation of 2,6-dimethylcyclopropyl-benzene takes place 85% at the 3 position. Significantly, the cyclopropane ring in their system also is though to be predominantly in the worst possible conformation for conjugative interaction. In such a situation, the observed domination of directive effects by ordinary alkyl groups is compatible with the previously mentioned relative electronegativity of cyclopropane exocyclic orbitals.[14]

Structure Assignments

The pmr τ values of aromatic protons selected to assign structures of the isomeric nitrocyclopropyl aromatic systems described in this study are listed in Table IV. Coupling constants in all cases were observed to be ca. 2.5 cps for J_{ab} and 8–9 cps for J_{bc} (partial structure B).
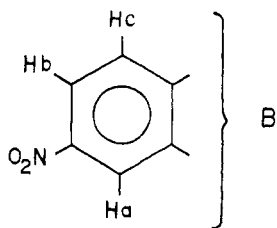
In the β-nitrocyclopropyl aromatic series, anisotropic deshielding effects of the cyclopropane ring, which occur when a proton is near a cyclopropane edge,[15a] are seen in the H_a τ values for β-NO$_2$-IV and β-NO$_2$-VIII (1.97 and 1.83). These effects can account for the downfield shifts in these peaks (-0.15 and -0.27 ppm) relative to the H_a values noted for β'-NO$_2$-IV and β'-NO$_2$-VIII. In the β' series, H_c values for β'-NO$_2$-IV

(21) R. C. Hahn, T. F. Corbin, and H. Shechter, *J. Am. Chem. Soc.,* **90,** 3404 (1968).

Table IV. Chemical Shifts (τ, CDCl$_3$) of Nitrocyclopropyl Aromatics

Compound	H_a	H_b	H_c
β-Nitroindan	2.09	2.05	2.74
β-NO$_2$-IV	1.97	2.11	2.83
β'-NO$_2$-IV	2.12	2.05	2.68
β-NO$_2$-V	2.62	2.12	2.80
β'-NO$_2$-V	2.00	2.04	3.31
β-Nitrotetralin	2.30	2.32	2.95
β'-NO$_2$-VI	2.13	2.07	2.65
β'-NO$_2$-VII	2.10	2.15	3.28
β-Nitrobenzosuberan	1.99	2.07	2.77
β-NO$_2$-VIII	1.83	2.02	2.82
β'-NO$_2$-VIII	2.10	2.01	2.58

and β'-NO$_2$-VIII (2.68 and 2.58) are shifted downfield by essentially the same amounts (-0.15 and -0.24 ppm) relative to H_c values listed for β-NO$_2$-IV and β-NO$_2$-VIII. The H_c value for β'-NO$_2$-VI is assumed to be similarly affected by cyclopropane deshielding. Strong cyclopropane anisotropic shielding effects, arising when a proton is near a cyclopropane face,[22] are reflected in the H_c values for β'-NO$_2$-V and β'-NO$_2$-VII, and in the H_a value for β-NO$_2$-V.

A recent report of unusual anisotropic carbonyl deshielding effects in the pmr spectra of *ortho*-substituted acylanilines[23] prompts mention of nitroacetanilides C and D, isolated in the course of the corresponding "iso processes" (Chart II). Cyclopropane anisotropy effects on the α proton in these two compounds (deshielding in C, shielding in D) confirm the aromatic proton resonance assignments (τ values shown), since the α' proton should have an essentially constant value. All of the cyclopropane anisotropy
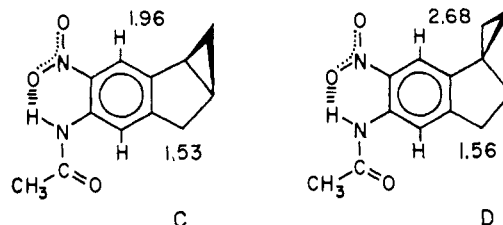
effects noted above are in keeping with estimated preferred molecular conformations, described previously in terms of θ values.

Ultraviolet Spectra

Observed absorption maxima and extinction coefficients for the nitrocyclopropyl aromatics to be discussed and other nitro compounds of interest are listed in Table V. Spectra from β-nitro series compounds are shown in Figure 1; spectra in (cyclo) hexane were chosen to minimize band-broadening solvent effects[20] to facilitate observation of the weak long-wavelength absorption band seen for some members of the series. Attention is centered first on the more intense λ_{max} at 272–275 mμ. There is no great difference in the position of this band for β-nitroindan, β-nitrotetralin, β-nitrobenzosuberan, β-NO$_2$-IV, β-NO$_2$-V, and β-NO$_2$-VIII. We infer from these spectral similarities that there are minimal ring

(22) *Cf.* S. Forsén and T. Norin, *Tetrahedron Letters,* 2845 (1964).
(23) M. Zanger, W. W. Simmons, and A. R. Gennaro, *J. Org. Chem.,* **33,** 3673 (1968).

Table V. Values of λ_{max} (mμ) and ϵ_{max} for Various Nitro Aromaties

Compound	θ, deg	Cyclohexane[a]		95% EtOH[a]		
		λ_{max}, mμ	Log ϵ	λ_{max}, mμ	Log ϵ	$\Delta\lambda$
p-NO$_2$-III[c]		283	4.05	297	4.03	14
p-Nitroanisole[d]		293[b]	4.04	307	4.06	14
m-NO$_2$-III		260[b]	3.91	270	3.84	10
m-Nitroanisole[d]		260[b]	3.75	268	3.77	8
β-Nitroindan		273	3.94	282	3.90	9
β-Nitrotetralin		272	3.97	281	3.95	9
β-Nitrobenzosuberan		273	3.96	282	3.92	9
β-NO$_2$-V	0	275	3.85	282	3.80	7
β-NO$_2$-IV	25	275	3.89	282	3.84	7
β-NO$_2$-VIII	90	273	3.97	280	3.94	7
β'-NO$_2$-VIII	90	277	3.99	285	3.96	8
β'-NO$_2$-IV	25	287	3.98	301	3.94	14
β'-NO$_2$-VI	10	290	4.00	306	3.99	16
β'-NO$_2$-VII	10	292	3.99	306	3.98	14
β'-NO$_2$-V	0	293	3.97	313	3.96	20

[a] Except as noted. [b] Hexane. [c] Reported values in hexane are: λ_{max} 280 (log ϵ 4.04); L. A. Strait, R. Ketcham, D. Jambotkar, and V. P. Shah, *J. Am. Chem. Soc.*, **86**, 4628 (1964). [d] L. Lang, Ed., "Absorption Spectra in the Ultraviolet and Visible Region," Vol. VI, Academic Press, New York, N. Y., 1965.

Figure 2. Ultraviolet spectra (95% EtOH) of β'-nitro derivatives of IV, V, VI, and VIII.

size and strain effects on the energies of these transitions.[24]

It is also seen in Figure 1 that the cyclopropane ring, regardless of geometry, exerts little effect on the λ_{max} value of either the stronger or the weaker long-wavelength transition. Cyclopropane geometry in the β-nitro series does appear to affect long-wavelength ϵ_{max} values however. The weak band at *ca.* 310 mμ (λ_{max} estimated by rough reflection subtraction[20]) shows maximum intensity in β-NO$_2$-V ($\theta = 0°$), while the 275-mμ band for the same compound is the least intense in the series. As θ is increased through β-NO$_2$-IV and m-NO$_2$-III to β-NO$_2$-VIII, the 310-mμ band diminishes to a very weak shoulder, while the 273–275-mμ band increases to the intensity observed for the β-nitro reference systems.

Spectra from β'-nitro series compounds are shown in Figure 2; spectra in 95% ethanol were chosen to maximize λ_{max} differences. Three features contrasting with those of the β series may be noted. First, there is only one apparent long-wavelength absorption, regardless of cyclopropane geometry. Second, the ϵ_{max} value of this absorption remains nearly constant in the β'-nitro series. Finally, there is a clear trend to bathochromic shifts within the series from β'-NO$_2$-VIII ($\theta = 90°$) to β'-NO$_2$-V ($\theta = 0°$).

The bathochromic shifts in the β'-nitro series and the weak band hyperchromic effects in the β-nitro series appear to be primarily functions of increasingly favorable cyclopropane geometry for conjugation with the adjacent π system. Significantly, the weak band in the β-nitro series (nitro *meta* to cyclopropyl) appears at a longer wavelength than the most bathochromically shifted band in the β'-nitro series (nitro *para* to cyclopropyl).[25]

The solvent shifts ($\Delta\lambda$'s) seen in Table V are attributed to the greater ability of the more polar, protic solvent

(24) In contrast, λ_{max} for β-nitrobenzocyclobutene (267 mμ in n-heptane) is clearly affected by ring strain; J. B. F. Lloyd and P. A. Ongley, *Tetrahedron*, **20**, 2185 (1964).

(25) All of the features of the uv spectra of the cyclopropylnitro compounds described in this paper have been correlated in a theoretical analysis to be reported elsewhere.
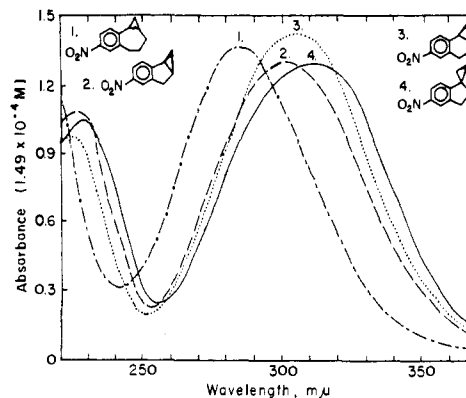
to stabilize the excited state, relative to the ground state. The greater solvent shifts for most p-cyclopropylnitro compounds are ascribed to excited-state protonation of the nitro group,[26,27] thereby increasing the electron deficiency of the chromophore and the conjugative response of the cyclopropyl group where permitted by its geometry.

It is felt that the data presented above justify the following conclusions. First, absence of significant spectral differences in cyclopropyl aromatic hydrocarbons compared with suitable standards (Tables I–III) may be regarded as a consequence of the minimal electron-attracting ability of the chromophore in these systems, in contrast to the nitro derivatives. Second, cyclopropane conjugation in cyclopropyl aromatic systems is a spectroscopically detectable function of cyclopropane geometry if the interacting chromophore is sufficiently electron-attracting.

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 Baird-Atomic, Beckman D.B., or Perkin-Elmer Infracord Model 137. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Scandinavian Microanalytical Laboratory, Herlev, Denmark.

1,3-Dibromo-1-(α-naphthyl)propane. A mixture of 1-bromo-3-(α-naphthyl)propane[28] (22 g, 67 mmol), N-bromosuccinimide (NBS) (13 g, 74 mmol),[29] benzoyl peroxide (0.2 g), and dry carbon tetrachloride (100 ml) was heated to reflux, with mechanical stirring. After 1 hr, hydrogen bromide fumes were detected, and the mixture was allowed to cool to room temperature. Unreacted NBS (2 g) and succinimide were filtered off and washed with carbon tetrachloride (20 ml). Combined liquid portions were concentrated at a bath temperature of 45–50°[30] and aspirator pressure. Remaining solvent was removed at 0.2 mm, leaving crude solid 1,3-dibromo-1-(α-naphthyl)propane. Recrystallization (benzene–hexane) and vacuum sublimation yielded 16.5 g (75%) of pale yellow crystals, mp 70–71.5°.

(26) R. Hurley and A. C. Testa, *J. Am. Chem. Soc.*, **89**, 6917 (1967).

(27) The concept of varying steric hindrance to solvation, effectively applied to explain the order of excitation energies in p-nitroalkylbenzenes (see Table II, footnote e), does not appear to play a major role here.

(28) R. Huisgen and U. Rietz, *Tetrahedron*, **2**, 271 (1958).

(29) Best results were obtained with NBS freshly prepared and vacuum dried over phosphorus pentoxide immediately before use.

(30) Higher temperatures caused darkening of the residue and evolution of hydrogen bromide.

α-**Cyclopropylnaphthalene** (I). Zinc powder (20 g, 0.3 mol) was washed consecutively with 3% aqueous hydrochloric acid (three 50-ml portions), 2% aqueous copper sulfate (two 50-ml portions), and DMF (dimethylformamide) (two 50-ml portions), and the resulting Zn–Cu couple[31] was mixed with freshly distilled DMF (180 ml). The mixture was cooled to 7°, and a solution of 1,3-dibromo-1-(α-naphthyl)propane (16.5 g, 50 mmol) in DMF (20 ml) was added dropwise with stirring. After addition was completed, the solution was allowed to warm to room temperature, whereupon a spontaneous further rise to 40° occurred. Stirring was continued for 1.5 hr. The mixture was poured into water (500 ml) and steam distilled until the condensate was homogeneous. An ether extract of the distillate was washed and dried, and the ether was removed. Distillation of the remaining liquid gave colorless I (4.0 g, 24 mmol, 58%), bp 100–103° (1.2 mm), n^{20}D 1.6158, essentially pure by vpc analysis; pmr (CCl₄) τ 1.80 (1 H, multiplet, *peri* H), 2.60 (6 H, multiplet, all other aromatic H's), 7.85 (1 H, multiplet, cyclopropyl methine H), and 9.25 (4 H, multiplet, cyclopropyl –CH₂–).

Anal. Calcd for $C_{13}H_{12}$: C, 92.81; H, 7.19. Found: C, 92.79; H, 7.19.

α-Cyclopropylnaphthalene has no observable tendency to discolor or polymerize on storage over a period of months. The picrate (yellow crystals from 95% ethanol) has mp 92–93°.

3-(β-**Naphthyl**)**propanol.** Portions of 3-(β-naphthyl)propionic acid totaling 34 g (0.17 mol)[32] were extracted (2 hr) from a Soxhlet thimble into a solution of lithium aluminum hydride (15.5 g, 0.41 mol) in refluxing ether (500 ml). Excess hydride was decomposed by ethanol, and 10% aqueous sodium hydroxide (400 ml) was added to the mixture. The organic layer was separated, dried, and stripped of ether. Distillation of the remaining liquid afforded 21 g (65%) of colorless solid product, mp 32–33°, bp 123–135° (0.25 mm); lit.[33] mp 33°.

1-**Bromo**-3-(β-**naphthyl**)**propane.** A mixture of 3-(β-naphthyl)-propanol (21 g, 0.11 mol) 48% aqueous hydrobromic acid (40 ml) and red phosphorus (0.7 g) was refluxed 6 hr. Concentrated sulfuric acid (7 ml) was added and the mixture refluxed 6 hr more. Organic material was taken up in ether and dried. Solvent was removed and the residue distilled, yielding 23 g (82%) of the bromide as a pale yellow solid. Vacuum sublimation gave a colorless sample, mp 42–43°. Elemental and infrared analysis indicated the presence of the parent alcohol.

Anal. Calcd for $C_{13}H_{12}Br$: C, 62.27; H, 5.26; Br, 32.07. Found: C, 64.61; H, 5.66; Br, 29.79.

1,3-**Dibromo**-1-(-β-**naphthyl**)**propane.** 1-Bromo-3-(β-naphthyl)-propane (23 g, 0.09 mol) was allowed to react with N-bromosuccinimide (18.6 g, 0.1 mol) and benzoyl peroxide (0.3 g) as described for the α isomer. Solvent was removed at atmospheric pressure. The crude reaction product was crystallized (benzene–hexane) and vacuum sublimed [90° (1 mm)] to give 26.5 g (90%) of pale yellow crystals, mp 72–75°.

Anal. Calcd for $C_{13}H_{12}Br_2$: C, 47.59; H, 3.69; Br, 48.72. Found: C, 48.04; H, 3.83; Br, 48.02.

β-**Cyclopropylnaphthalene** (II). 1,3-Dibromo-1-(β-naphthyl)propane (26.5 g, 0.081 mol) was treated with zinc–copper couple by the procedure described for prepatation of α-cyclopropylnaphthalene. After removal of most of the ether from a dried extract of the steam distillate, the residue was stripped of remaining solvent by evacuation at room temperature, leaving 3.5 g (25%) of crystalline II, mp 31–33°. Vacuum sublimation [45° (1 mm)] afforded a purer sample, mp 34–35°; pmr (CCl₄) τ 2.67 (7 H, multiplet, aromatic H's), 8.05 (1 H, multiplet, cyclopropyl methine H), and 9.13 (4 H, multiplet, cyclopropyl –CH₂–).

Anal. Calcd for $C_{13}H_{12}$: C, 92.81; H, 7.19. Found: C, 92.74; H, 7.29.

β-Cyclopropylnaphthalene, though solid, has a much more intense odor than the α isomer; the picrate (orange-yellow needles from 95% ethanol) has mp 100.5–101.5°.

m-**Nitrocyclopropylbenzene.** This compound was prepared from *p*-cyclopropylacetanilide[21] through the standard sequence of nitration, basic hydrolysis, diazotization, and hypophosphorous acid deamination. The product so obtained was a yellow liquid, bp 98–98.5° (1 mm), n^{21}D 1.5698, essentially pure by vpc analysis.

Anal. Calcd for $C_9H_9NO_2$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.33; H, 5.55; N, 8.44.

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(31) This is a modification of the procedure of G. F. Hennion and J. J. Sheehan, *J. Am. Chem. Soc.*, **71**, 1964 (1949).

(32) F. Mayer and A. Sieglitz, *Chem. Ber.*, **55**, 1855 (1922).

(33) S. Searles, *J. Am. Chem. Soc.*, **73**, 125 (1951).

m-Nitrocyclopropylbenzene has characteristic ir absorption (neat, NaCl) at 12.60, 13.70, and 14.84 mμ (compare *m*-nitroethylbenzene at 12.50, 13.75, and 14.95 mμ); pmr (neat) τ 2.16 (2 H, multiplet, H's *ortho* to NO₂), 2.68 (2 H, multiplet, H's *meta* and *para* to NO₂), 8.08 (1 H, multiplet, cyclopropyl methine H), and 9.12 (4 H, multiplet, cyclopropyl –CH₂–).

4-**Nitro**-1,1a,6,6a-**tetrahydrocycloprop**[*a*]**indene** (β'-NO₂-IV). A solution of acetyl nitrate made by mixing 100% nitric acid (5 g, 0.8 mol) and acetic anhydride (10.2 g) was added in 45 min to a stirred solution of IV[11] (10 g, 77 mmol) in acetic anhydride (10 ml) maintained at 7–13°. After another 1.5 hr the reaction mixture was poured into cold water (400 ml). The dark red oil which separated was taken up in ether and washed with dilute aqueous potassium carbonate until the aqueous layer was almost colorless. The ether solution was dried and stripped of solvent, and the oily residue (6.1 g) was dissolved in benzene (6 ml). This solution was chromatographed on silica gel using benzene as the eluent. Removal of solvent from the eluate gave a mixture (3.5 g) of mononitro isomers, from which some β'-NO₂-IV could be separated by crystallization from hexane–benzene. Vacuum sublimation [60–65° (3–5 mm)] gave almost colorless crystals, mp 76–76.5°. Assignment of structure is based on pmr and uv spectra (see Discussion section); distinctive ir bands appear at 925, 835, 810, 800, and 750 cm⁻¹ (compare β-nitro isomer, below).

Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.45; H, 5.32; N, 7.96.

Preparation of 3-Nitro-1,1a,6,6a-tetrahydrocycloprop[*a*]**indene (β-NO₂-IV). 4-Amino-1,1a-6,6a-tetrahydrocycloprop**[*a*]**indene (β'-NH₂-IV).** Hydrogenation of β'-NO₂-IV (2.50 g, 14 mmol) was performed in a medium-pressure Parr apparatus at room temperature using 150 ml of 95% ethanol and 0.15 g of platinum oxide. After hydrogen uptake (slightly more than theoretical) had practically ceased, the catalyst was filtered off and the solvent evaporated, leaving a pale yellow solid. Recrystallization from hexane gave 1.95 g (94%) of colorless crystals, mp 68–68.5°; pmr (CDCl₃) τ 6.96 (2 H, singlet, broad, NH₂); ir (KBr) 3400, 3300, and 1660 cm⁻¹ (NH₂).

3-**Nitro**-4-**acetamido**-1,1a,6,6a-**tetrahydrocycloprop**[*a*]**indene** (β-NO₂-β'-AcNH-IV). To a solution of β'-NH₂-IV (1.95 g, 13.4 mmol) in 16 ml of acetic anhydride at 20° was added dropwise 0.882 g of anhydrous nitric acid (0.014 mol) in 1.5 ml of acetic anhydride (premixed at room temperature). The reaction mixture was stirred for 1 hr at 18–20°, poured onto ice, and made basic with concentrated aqueous sodium hydroxide. The basic water solution was extracted with ether and the combined ether portions were washed with water and dried over anhydrous potassium carbonate.

After filtration and solvent removal, the yellow solid residue was recrystallized from ether to yield 2.077 g of β-NO₂-β'-AcNH-IV, mp 112–114°; pmr (CDCl₃) τ −0.27 (1 H, singlet, broad, –NH–), 1.53 (1 H, singlet, α'-H), and 1.96 (1 H, singlet, α-H); ir (KBr) 3310 (NH), 1685 (C=O), 1580 and 1315 cm⁻¹ (–NO₂).

Anal. Calcd for $C_{12}H_{12}N_2O_3$: C, 62.06; H, 5.21; N, 12.06. Found: C, 62.07; H, 5.20; N, 11.87.

The mother liquor from the above crystallization was put on a silica gel column and developed with 5–10% ether–hexane. Two yellow bands separated cleanly. The first band, on elution and solvent removal, gave 700 mg of material identical with the previously crystallized β-nitro isomer. Similar treatment of the second yellow band afforded 110 mg of the assumed α'-nitro isomer, mp 126.5–128°.

3-**Nitro**-4-**amino**-1,1a,6,6a-**tetrahydrocycloprop**[*a*]**indene** (β-NO₂-β'-NH₂-IV). A portion of β-nitro-β'-amide (1.00 g, 4.3 mmol) was hydrolyzed by solution in aqueous methanolic potassium hydroxide for 2 hr at room temperature. Recrystallization of the crude product (ethanol–water) gave the β-nitro-β'-amine as orange crystals (773 mg, 95%), mp 101–102.5°; pmr (CDCl₃) τ 2.03 (1 H, singlet, α-H), 3.40 (1 H, singlet, α'-H), and 3.93 (2 H, broad, –NH₂); ir (KBr) 3400, 3300, and 1640 (–NH₂), and 1570 and 1305 cm⁻¹ (–NO₂).

Anal. Calcd for $C_{10}H_{10}N_2O_2$: C, 63.15; H, 5.30; N, 14.73. Found: C, 62.90; H, 5.44; N, 14.62.

A sample of β-NO₂-β'-NH₂-IV (770 mg, 4 mmol) was mixed with concentrated sulfuric acid (4.06 g, 40 mmol) in 20 ml of water, and sodium nitrite (299 mg, 4.3 mmol) in water (3 ml) was added in 15 min with stirring at 0–5°. After 45 min more, chilled 50% hypophosphorous acid (7.92 g, 60 mmol) was poured in. The mixture was allowed to react for 1 hr at 0–5° and refrigerated 24 hr.

The mixture was extracted with ether and the combined orange ether portions were washed consecutively with 1 N aqueous sodium hydroxide and water. The ether layer was dried over anhydrous

potassium carbonate and filtered and the ether removed leaving a red residue. Column chromatography (silica gel, pentane eluent) separated a yellow band which yielded a yellow solid. Recrystallization from hexane gave 300 mg (43%) of pale yellow β-NO$_2$-IV, mp 45–46.5°.

Pmr features are presented in the Discussion. Distinctive ir bands (KBr) appear at 820, 791, and 735 cm^{-1}.

Anal. Calcd for C$_{10}$H$_9$NO$_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.40; H, 5.22; N, 7.91.

Preparation of 5'-Nitrospiro[cyclopropane-1,1'-indan] (β'-NO$_2$-V). 1-Methyleneindan. Dried methyltriphenylphosphonium bromide (217 g, 0.62 mol) was added to a stirred solution of *n*-butyllithium (260 ml of a 22% hexane solution, 0.6 mol) in dry ether (1200 ml). After 0.5 hr, 1-indanone (70 g, 0.54 mol) in ether (250 ml) was added dropwise. The mixture was stirred 40 hr at 35° and filter aid was added. The filtrate was extracted with 1 *N* aqueous sodium hydroxide until the aqueous extract was no longer red. The ether solution was further washed and dried, and solvent removed. Distillation of the residue at 26–28° (0.2 mm) gave 22 g (34%) of colorless solid, mp 24.5–25°; lit.[11] bp 99.5–101.5° (29 mm).

The nmr spectrum of the alkene (CDCl$_3$) has peaks at τ 2.63 (1 H, multiplet, α aromatic H), 2.99 (3 H, unsymmetrical doublet, other aromatic H's), 4.61 and 5.03 (1 H each, multiplets, vinyl H's), and 7.37 (4 H, singlet, –CH$_2$–'s). Ir features match those previously reported.[11]

Spiro[cyclopropane-1,1'-indan] (V). A mixture of zinc–copper couple from 26.2 g (0.4 mol) of 10 mesh zinc, diiodomethane (82.5 g, 0.3 mol), and dry ether (250 ml) was allowed to react with 1-methyleneindan (9.0 g, 69 mmol) according to the published method.[11] Work-up and distillation gave the methylene adduct (4.0 g, 40%) as a colorless liquid fraction, bp 44–48° (1 mm).

The product has nmr peaks (neat) at τ 3.00 (3 H, unsymmetrical doublet, β, β', α' H's), 3.53 (1 H, multiplet, α H), 7.13 (2 H, triplet, benzylic H's), 8.10 (2 H, triplet, H's adjacent to cyclopropane), and 9.23 (4 H, singlet, cyclopropyl H's).

β'-NO$_2$-V. To a solution of V (1.023 g, 7.1 mmol) in acetic anhydride (2 ml) was added a solution of 100% nitric acid (447 mg, 7.1 mmol) in 2 ml of acetic anhydride (premixed at 15–20°) over 1 hr at 25°. After 0.5 hr more, the mixture was poured into ice water, and extracted with ether. The ether solution was washed thoroughly with 3% aqueous potassium carbonate and then with water, and dried over magnesium sulfate. After removal of solvent the residue was put on a silica gel column and developed with hexane. Impure β'-NO$_2$-V (294 mg) was eluted; repeated recrystallizations (hexane) yielded 87 mg of pale yellow solid, mp 81–82.5°. The pmr spectrum (CDCl$_3$), in addition to aromatic features used for the structure assignment (see the Discussion), has high-field peaks resembling those of the parent V, but shifted downfield by 0.23–0.28 ppm. Distinctive ir bands (KBr) appear at 895 and 748 cm^{-1} (compare β-nitro isomer, below).

Anal. Calcd for C$_{11}$H$_{11}$NO$_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 70.07; H, 5.88; N, 7.26.

5'-Acetamidospiro[cyclopropane-1,1'-indan] (β'-AcNH-V). A sample of β'-NO$_2$-V (1.704 g, 9 mmol) was hydrogenated as described for β'-NO$_2$-IV. An air-sensitive oil was isolated and immediately acetylated with acetic anhydride to give, after recrystallization from benzene–hexane, 1.62 g (90%) of β'-AcNH-V as colorless flakes, mp 131.5–133°; pmr (CDCl$_3$) τ 1.32 (1 H, broad, –NH–); ir (KBr) 3250 (NH) and 1660 cm^{-1} (C=O).

Anal. Calcd for C$_{13}$H$_{15}$NO: C, 77.58; H, 7.51; N, 6.96. Found: C, 78.02; H, 7.43; N, 6.91.

6'-Nitro-5'-acetamidospiro[cyclopropane-1,1'-indan] (β-NO$_2$-β'-AcNH-V). A sample of β'-AcNH-V (1.445 g, 7 mmol) was dissolved in acetic anhydride (20 ml) at 25–30°, and premixed 100% nitric acid–acetic anhydride (8 mmol in 2 ml) was added in 15 min. After 0.5 hr more, the mixture was worked up as described for previous nitrations to give a dark brown solid. When a hexane extract of this material was chromatographed on silica gel (developed with 5–10% ether–hexane), two yellow bands separated cleanly. Elution of the first band gave 700 mg of β-nitro isomer as yellow needles, mp 120–121.5°; pmr (CDCl$_3$) τ −0.23 (1 H, singlet, broad, –NH–), 1.56 (1 H, singlet, α'-H), 2.68 (1 H, singlet, α-H); ir (KBr) 3280 (NH), 1685 (C=O), and 1575 and 1320 cm^{-1} (–NO$_2$).

Anal. Calcd for C$_{13}$H$_{14}$N$_2$O$_3$: C, 63.40; H, 5.73; N, 11.38. Found: C, 63.61; H, 5.69; N, 11.19.

Similarly, from the second band there was obtained 25 mg of the assumed α'-nitro isomer, mp 182–184° (softening at 165°).

6'-Nitro-5'-aminospiro[cyclopropane-1,1'-indan] (β-NO$_2$-β'-NH$_2$-V). Hydrolysis of β-NO$_2$-β'-AcNH-V (545 mg, 2.2 mmol) and work-up as described for hydrolysis of β-NO$_2$-β'-AcNH-IV yielded 460 mg (98%) of β-NO$_2$-β'-NH$_2$-V as red needles, mp 163–164°; pmr (CDCl$_3$) τ 2.61 (1 H, singlet, α-H), 3.39 (1 H, singlet, α'-H), and 4.05 (2 H, broad, –NH$_2$); ir (KBr) 3420 and 3310 (–NH$_2$), and 1575 and 1305 cm^{-1} (–NO$_2$).

Anal. Calcd for C$_{11}$H$_{12}$N$_2$O$_2$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.63; H, 5.89; N, 13.55.

6'-Nitrospiro[cyclopropane-1,1'-indan] (β-NO$_2$-V). The procedure described for preparation of β-NO$_2$-IV was used, with 440 mg (2 mmol) of β-NO$_2$-β'-NH$_2$-V, 2.04 g of concentrated sulfuric acid in 20 ml of water, 116 mg (2.4 mmol) of sodium nitrite, and 4.16 g (31.5 mmol) of 50% hypophosphorous acid. Incomplete diazotization, attributed to insolubility of the nitroamine sulfate, necessitated a second, similar deamination on recovered starting material. Silica gel chromatography (hexane eluent) and short-path distillation (0.3 mm) of combined eluates from the two runs yielded 36 mg of β-NO$_2$-V as pale yellow crystals, mp 40.5–41.5°. The structure was confirmed by the pmr and uv spectra (Discussion section). Characteristic ir bands (KBr) appear at 1520, 1340, and 740 cm^{-1}.

Anal. Calcd for C$_{11}$H$_{11}$NO$_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 70.01; H, 5.68; N, 7.44.

Preparation of 4-Nitro-1a,2,3,7b-tetrahydro-1H-cyclopropa[a]-naphthalene (β'-NO$_2$-VI). 1a,2,3,7b-Tetrahydro-1H-cyclopropa[a]-naphthalene (VI). A solution of diiodomethane (100 g, 0.37 mol) and 1,2-dihydronaphthalene[34] (30 g, 0.23 mol) in 50 ml of ether was added dropwise to a suspension of zinc–copper couple[35] (27 g, 0.42 mol) in 200 ml of ether. The stirred mixture was refluxed 30 hr, allowed to cool, and filtered through Celatom. The filtrate was successively washed with saturated aqueous ammonium chloride, 10% ammonium hydroxide, and saturated aqueous sodium chloride. Drying, removal of solvent, and distillation gave an impure colorless oil. Fractionation through a Teflon annular still gave a fraction, bp 48° (1 mm), which was further purified by chromatography on silver nitrate impregnated alumina[36] (hexane elution) and redistillation to afford 6.6 g (20%) of olefin-free VI; pmr (neat) τ 3.02 (4 H, multiplet, aromatic H), 7.70 (2 H, multiplet, benzylic –CH$_2$–), 8.40 (4 H, multiplet, cyclopropylcarbinyl –CH$_2$– and cyclopropyl methine H's), and 9.38 (2 H, quartet, cyclopropyl –CH$_2$–); ir (NaCl) 1485, 905, 835, 798, 758, and 740 cm^{-1}. Other constants match reported values.[11]

β'-NO$_2$-VI. Hydrocarbon VI (5.76 g, 40 mmol) in acetic anhydride (20 ml) was nitrated as described for V, using 100% nitric acid (3.15 g, 50 mmol) in acetic anhydride (6 ml). Work-up gave a dark oil containing approximately equal amounts of α- and β'-nitro isomers (vpc analysis, 5 ft × $^1/_8$ in. column, Apiezon L on Chromosorb W, 240°). Combined crude product (14 g) of two equivalent runs was chromatographed on silica gel (600 g). Elution with hexane afforded first α-NO$_2$-VI (pale yellow oil, not further characterized).

Finally, fractions containing at least 95% β'-NO$_2$-VI were recrystallized from hexane to afford 2.3 g of this isomer as almost colorless crystals, mp 45.0–46.5°. The structure assignment was based on uv and aromatic pmr absorption bands (Discussion section). Characteristic ir bands (KBr) appear at 1500, 1340, 828, 798, 751, and 732 cm^{-1}.

Anal. Calcd for C$_{11}$H$_{11}$NO$_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 70.07; H, 6.08; N, 7.30.

Preparation of 6'-Nitrospiro[cyclopropane-1,1'-tetralin] (β'-NO$_2$-VII). 1-Methylenetetralin. Sodium hydride (17.6 g, 0.73 mol) in 400 ml of dimethyl sulfoxide (DMSO) was kept at 75–80° for 45 min and then cooled. Triphenylmethylphosphonium bromide[37] (261.6 g, 0.73 mol) in warm DMSO (800 ml) was added dropwise. The mixture was stirred 15 min and α-tetralone[38] (116.8 g, 0.80 mol) dripped in. After overnight stirring the solution was brought to 60° for 1 hr, and poured into 2 l. of cold water. Precipitate was filtered out, and the organic filtrate was extracted into petroleum ether (bp 30–60°). Distillation of the dried solution, after removal of solvent, yielded 29.6 g (26%) of 1-methylenetetralin, bp 58° (0.5 mm); lit.[39] 103° (14 mm); pmr (neat) τ 2.50 (1 H, multiplet,

(34) Prepared by the procedure of A. Mizote, T. Tanoka, T. Higashimura, and S. Okamura, *J. Polymer Sci., Part A-1*, **4**, 869 (1966).

(35) E. LeGoff, *J. Org. Chem.*, **29**, 2084 (1964).

(36) L. R. Chapman and D. F. Kuemmel, *Anal. Chem.*, **37**, 1598 (1965).

(37) G. Wittig and U. Schoellkopf, *Org. Syn.*, **40**, 67 (1960).

(38) C. E. Olson and A. R. Bader, *ibid.*, **35**, 95 (1955).

(39) G. Schroeter, *Chem. Ber.*, **58**, 713 (1925).

α-H), 3.02 (3 H, multiplet, other aromatic H's), 4.64 and 5.17 (1 H each, multiplets, vinyl H's), 7.27 (2 H, triplet, benzylic H's), 7.54 (2 H, triplet of doublets, allylic H's), and 8.25 (2 H, quintet, remaining -CH₂-); ir (neat, NaCl) 1625 (PhC=C) and 883 cm⁻¹ (=CH₂).

Spiro[cyclopropane-1,1′-tetralin] (VII). Zinc–copper couple was made by a modification of published procedures.[40] Zinc dust (65.4 g, 1.0 mol) was washed consecutively with 3% hydrochloric acid (three 100-ml portions), water (five 100-ml portions), 2% aqueous copper sulfate (two 100-ml portions), water (five 100-ml portions), and absolute ethanol (three 100-ml portions). The couple then was washed into the reaction vessel with 100 ml of benzene, solvent was distilled off under dry nitrogen, and 660 ml of dry ether was added. Diiodomethane (220 g, 0.82 mol) was added slowly with stirring, and the mixture was refluxed 0.5 hr. 1-methylenetetralin (59.2 g, 0.41 mol) was added dropwise to the cooled, stirred suspension, which then was refluxed 20 hr. Work-up as for synthesis of VI and distillation gave 48.6 g (75%) of 95% pure VII (vpc), bp 56–57° (0.4 mm). Spinning-band fractionation afforded analytically pure material; pmr (neat) τ 3.10 (3 H, multiplet, aromatic H's), 3.54 (1 H, multiplet, α-H; compare starting material), 7.30 (2 H, triplet, benzylic H's), ~8.35 (4 H, multiplet, other 6-ring -CH₂-'s), 9.30 (4 H, A₂B₂ doublet with further splitting, cyclopropyl -CH₂-'s); ir (neat, NaCl) 1480, 752, and 721 cm⁻¹.

Anal. Calcd for C₁₂H₁₄: C, 91.08; H, 8.92. Found: C, 90.84; H, 9.15.

6′-Nitrospiro[cyclopropane-1,1′-tetralin] (β′-NO₂-VII). Hydrocarbon VII (6.32 g, 40 mmol) in acetic anhydride (20 ml) was nitrated as described for V, using 100% nitric acid (3.15 g, 50 mmol) in acetic anhydride (6 ml). Work-up gave a dark oil containing α- and β′-mononitro products as well as considerable starting material (vpc analysis). Silica gel chromatography (hexane elution) allowed separation of 330 mg of assumed α-NO₂-VII (not further investigated) and 430 mg of β′-NO₂-VII, mp 95–96° after hexane recrystallization. The structure assignment is based on pmr and uv spectra (see Discussion); β′-NO₂-VII has characteristic ir bands (KBr) at 1500, 910, 830, 791, and 745 cm⁻¹.

Anal. Calcd for C₁₂H₁₃NO₂: C, 70.91; H, 6.45; N, 6.89. Found: C, 70.71; H, 6.55; N, 6.89.

6,7,8,9-Tetrahydro-5H-benzocycloheptene (Benzosuberan). A solution of 6,7-dihydro-5H-benzocycloheptene[41] (4.30 g) in 95% ethanol was shaken under hydrogen in the presence of platinum oxide in a Parr hydrogenator. Work-up and distillation afforded 4.1 g (95%) of colorless liquid, mp 7° (macro); lit.[42] 6–7°, >99% pure by vpc analysis.

β-Nitrobenzosuberan. A solution of 100% HNO₃ (1.33 g, 2.11 mmol) in acetic anhydride (3 g) was added dropwise to a stirred solution of benzosuberan (1.90 g, 1.30 mmol) in acetic anhydride (5 g) maintained at 0–5°. Cooling was removed after addition was complete, whereupon the temperature rose to 34° before dropping to room temperature. The orange-brown product mixture was stirred 1 hr with water (40 ml), then extracted with ether. The residue after washing with water (two 50-ml portions), 5% aqueous sodium hydroxide (five 30-ml portions), and saturated aqueous sodium chloride (two 50-ml portions), drying over magnesium sulfate, and solvent stripping showed two peaks on vpc analysis (5 ft × ⅛ in. column, 10% Apiezon L on Chromosorb W, 230°), assumed to be α- and β-nitro isomers, area ratio 25:75. Chromatography of a hexane solution of the mixture on silica gel gave several fractions containing mostly α isomer, followed by fractions sufficiently rich in β isomer to allow further purification by recrystallization (hexane). A total of 1.3 g (52%) of nitro compounds was eluted. The pure β-nitro isomer (pale yellow crystals, mp 65.5–67°) was identified by its pmr spectrum (CDCl₃): τ 7.10 (multiplet, 4 H, benzylic CH₂'s) and ~8.30 (multiplet, 6 H, nonbenzylic CH₂'s) (see Table IV for aromatic region).

Anal. Calcd for C₁₁H₁₃NO₂: C, 69.09; H, 6.85; N, 7.33. Found: C, 69.38; H, 7.10; N, 7.05.

1,1a-2,3,4,8b-Hexahydrobenzo[a]cyclopropa[c]cycloheptene (VIII). A zinc–copper couple (27 g, 0.39 mol) was made as described for preparation of VII. Dry ether (150 ml) and a few iodine crystals were added. A solution of methylene iodide (94 g, 0.35 mol) and 6,7-dihydro-5H-benzocycloheptene[41] (28.8 g, 0.20 mol) in ether (30 ml) was added all at once, with vigorous stirring. Stirring

and gentle reflux were maintained 88 hr. Work-up as in synthesis of VI and distillation of the crude product gave 27.8 g of colorless liquid, bp 63–65° (0.7 mm), shown to be 60% VIII by vpc analysis (5-ft column, 15% Carbowax 20M, 200°). A column of silica gel (Davison 950, 60–200 mesh, 200 g) impregnated with silver nitrate (107 g) was moistened with hexane (100 ml), and a 14-g portion of the neat Simmons–Smith mixture was put on. Elution with hexane provided fractions as follows: fraction 1 (125 ml), nil; fraction 2 and 3 (50-ml each), >99% pure VIII; fraction 4 (1000 ml), >99% pure VIII. Fractions 2–4 were combined and stripped of solvent, and the residue was distilled to afford 7.03 g of essentially pure VIII, bp 65–66° (0.9 mm); pmr (CDCl₃) τ 2.6–3.1 (4 H, multiplet, aromatic H's), 6.67 (1 H, uneven sextet, benzylic H),[43] 7.52 (1 H, quartet further split, benzylic H),[43] 7.8–8.7 (4 H, overlapping multiplets, -CH₂CH₂-), 8.9–9.3 (2 H, multiplet, cyclopropyl methine H's), and 9.5–9.85 (2 H, multiplet, cyclopropyl -CH₂-); ir (neat, NaCl) 1028, 790, and 760 cm⁻¹.

Anal. Calcd for C₁₂H₁₄: C, 91.08; H, 8.92. Found: C, 91.37; H, 8.87.

Nitration of VIII. A solution of 100% nitric acid (3.78 g, 6.0 mmol) in acetic anhydride (12 g) was added over 15 min to a stirred solution of hydrocarbon VIII (6.32 g, 4.0 mmol) in acetic anhydride (10 g) maintained at 21–25°. The mixture was stirred 25 min at 20–22° after complete addition, then poured into water (150 ml) and stirred 4.5 hr. Extraction into ether preceded washing with water (one 100-ml portion), 5% aqueous sodium hydroxide (five 100-ml portions), and saturated aqueous sodium chloride (three 50-ml portions), drying over magnesium sulfate, and solvent stripping. Vpc analysis (Apiezon L, 240°) of the residue showed three peaks having relative areas of 95:43:133. The mixture was adsorbed on sufficient silica gel to be free flowing, and placed as adsorbed on a silica gel column (4 × 50 cm). Elution with hexane provided *ca.* 100 mg of starting material, followed by a few essentially pure, crystalline fractions of a nitro isomer corresponding to the second peak on the vpc scan. Recrystallization from hexane provided pale yellow crystals, mp 53.5–54°, assigned the structure 5-nitro-1,1a,2,3,4,8b - hexahydrobenzo[a]cyclopropa[c]cycloheptene (α′-NO₂-VIII) on the basis of the pmr spectrum (CDCl₃): τ 2.40 (1 H, doublet, β′-H), 2.43 (1 H, doublet, α-H), 2.87 (1 H, triplet, β-H), 6.5–7.3 (2 H, multiplet, benzylic H's), 7.7–8.4 (4 H, overlapping multiplets, -CH₂CH₂-), 8.7–9.3 (2 H, multiplet, cyclopropyl methine H's), 9.4–9.8 (2 H, multiplet, cyclopropyl -CH₂-). The two benzylic protons in α′-NO₂-VIII have much more nearly similar chemical shifts than those of the parent hydrocarbon VIII or the β- and β′-nitro derivatives (*vide infra*).[43] Characteristic ir peaks (CHCl₃) were found at 1525, 1349 (NO₂), 858, and 806 cm⁻¹. The last two bands are diagnostic for the presence of α′-NO₂-VIII in isomeric mixtures. Absence of β and β′ isomers was indicated by the absence of absorption at 1587, 1088, 905–910, and 833 cm⁻¹.

Anal. Calcd for C₁₂H₁₃NO₂: C, 70.91; H, 6.45; N, 6.89. Found: C, 70.69; H, 6.53; N, 6.90.

Later chromatographic fractions contained increasing proportions of vpc peak three. Pmr and ir analysis showed that this vpc peak contained both 6- and 7-nitro-1,1a-2,3,4,8b-hexahydrobenzo-[a]cyclopropa[c]cycloheptene (β- and β′-NO₂-VIII, respectively), and that the β′ isomer was eluted slightly faster. Fractions rich in the β-nitro isomer were recrystallized from hexane to give 500 mg of almost colorless material, mp 61–63.5°. (See the Discussion for pmr and uv data.)

In addition to characteristic NO₂ absorption, β-NO₂-VIII has diagnostic ir bands (CHCl₃) at 1266, 880, and 866 cm⁻¹.

Anal. Calcd for C₁₂H₁₃NO₂: C, 70.91; H, 6.45; N, 6.89. Found: C, 70.92; H, 6.65; N, 6.71.

Repeated silica gel–hexane chromatography of fractions rich in β′-NO₂-VIII and hexane recrystallization allowed isolation of this isomer as a pale yellow solid, mp 54–55°. The purity of this isomer was indicated in the ir spectrum by the absnce of diagnostic peaks for the α′ and β isomers, and by the aromatic region of the pmr spectrum (see Table IV, Discussion section.)

Anal. Calcd for C₁₂H₁₃NO₂: C, 70.91; H, 6.45; N, 6.89. Found: C, 71.19; H, 6.63; N, 6.61.

In addition to pmr and uv features noted in discussion, β- and β′-NO₂-VIII have nonaromatic pmr absorption patterns extremely similar to those of the parent hydrocarbon.

(40) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

(41) T. Fujita, *Yakugaku Zasshi*, **79**, 1192 (1959); *Chem. Abstr.*, **54**, 3352 (1960).

(42) G. Wittig, H. Eggers, and P. Duffner, *Ann. Chem.*, **619**, 10 (1958).

(43) Assignment of the benzylic protons in VIII and its α′-, β-, and β′-nitro derivatives was made possible by pmr spectral comparison with 4,4-dimethyl derivatives kindly provided by Professor R. Ketcham; see L. Martinelli, R. Ketcham, L. A. Strait, and R. Cavestri, *J. Am. Chem. Soc.*, in press.