of the nuclear spins. Alternatively, the efficiency of cage combination may be too high to allow sufficient S–T mixing to observe CIDNP. (b) The negative CIDNP results in various magnetic fields indicate that no S–T$_{-1}$ or S–T$_0$ mixing could be detected. (c) The fast electron transfer between TCNE$^{-\cdot}$ and TCNE in the order of 3×10^9 M^{-1} s^{-1} will also destroy spin correlation [cf. R. Kaptein, *Adv. Free-Radical Chem.*, **5**, 319 (1975)]. (d) Photo-CIDNP studies at low temperatures are in progress.
(52) Selectivities have been also measured for the same alkyltin compounds in electron transfer with iron(III) and iridate(IV)[30] and are diagnostic of the properties of the ion pair.[53]
(53) C. L. Wong, S. Fukuzumi, and J. K. Kochi, to be published.
(54) Cf. also (a) S. Boué, M. Gielen, J. Nasielski, J.-P. Lieutenant, and R. Spielmann, *Bull. Soc. Chim. Belg.*, **78**, 135 (1969); (b) for EI of related Me$_2$Hg see C. S. T. Cant, C. J. Danby, and J. H. D. Eland, *J. Chem. Soc., Faraday Trans. 2*, **71**, 1015 (1975).
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(56) Estimated in the fast exchange limit [cf. R. Chang and C. S. Johnson, Jr., *J. Chem. Phys.*, **46**, 2314 (1967)].
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Control of Regioselectivity in the Di-π-methane Rearrangement. Triplet-Sensitized Photoisomerization of Benzonorbornadienes Carrying Cyano Substituents in the Aryl and Vinyl Segments

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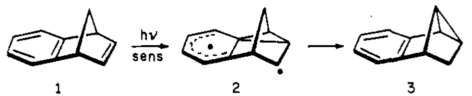
Abstract: Triplet-sensitized irradiation of 2-cyanobenzonorbornadiene (**10**) gives rise exclusively to 3-cyanotetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (**30**). This strong preference for benzo-vinyl bridging to C$_3$ has also been observed in the case of the four possible aryl-substituted dicyano derivatives. In all of these examples, striking regiospecificity is exhibited, despite untoward aryl polar effects in two examples. This bonding preference is shown to conform to the vacant orbital energies and shapes present in the starting benzonorbornadienes as calculated by STO-3G procedures and supported by photoelectron spectroscopy. The synthetic approaches to the polar substituted benzonorbornadienes are also detailed.

The high propensity of benzo-fused bicyclic dienes for triplet-sensitized di-π-methane rearrangement has been well established during the last decade.[1] With benzonorbornadiene (**1**) as the illustrative example, light-induced isomerization can be seen to involve initial intramolecular aryl-vinyl bridging and subsequent σ bond cleavage. Attachment of a substituent to the aromatic ring necessitates added consideration of regioselectivity. This is because **1** is a "doubly connected"[2] di-π-methane system, such that two regiochemically distinct bonding schemes are possible. Since conversion of biradical intermediates of type **2** to products has, in the many reported instances, been dominated completely by the exothermicity of rearomatization,[1] the observed product distribution is directly relatable to substituent control in the bridging step.



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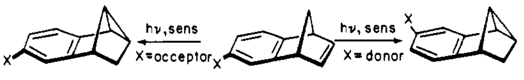
Previously, we reported on the striking control of bonding options observed during the photorearrangement of benzonorbornadienes substituted by electron donor and acceptor groups in the meta[3] and ortho positions.[4] In the case of meta acceptors, completely regiospecific para bridging was noted with ultimate formation of **4**. In contrast, meta donors directed matters predominantly through the alternate meta bridging channel to **5**. Interestingly, either type of ortho substituent promoted benzo-vinyl bridging preferentially to the adjacent (ortho) aryl carbon to deliver chiefly **7**. These results have been concisely accounted for in terms of an MO model which attributes considerable importance to benzene HOMO and LUMO polarization.[4a,5]



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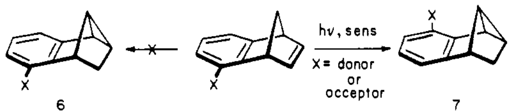

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The present research developed as a consequence of interest in the situation where two cyano substituents, one on the aryl ring and one on the vinyl moiety, would be allowed to vie for control of the bridging step. Hitherto, such competitive experiments had not been investigated.[6] The selection of cyano functionality for our initial studies was motivated by: (a) the unusually high regiocontrol noted earlier in the production of **4**-CN and **7**-CN, and (b) an earlier theoretical prediction that unsymmetrical substitution of the olefinic bond by an electron-withdrawing substituent should direct bridging away from the acceptor group because of the larger coefficient at the unsubstituted olefinic carbon in the LUMO.[5]

Results

Synthesis of the Dicyanobenzonorbornadienes. Access to the

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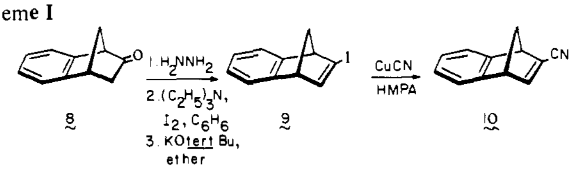
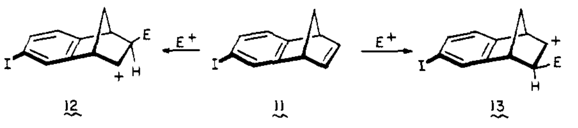
Scheme I



four dinitriles of interest first required development of methodology for positioning a cyano group at C-2 (or C-3) of the benzonorbornadiene ring system. The parent nitrile (**10**), required in its own right for exploratory photochemical investigation, was obtained in four steps from benzonorbornen-2-one (**8**, Scheme I). Conversion to the hydrazone and treatment of this derivative with iodine and triethylamine in benzene under inert atmosphere conditions[7] afforded predominantly the geminal diiodide. Exposure of this unpurified intermediate to potassium *tert*-butoxide in dry ether at 0 °C furnished **9**. Reaction of **9** with cuprous cyanide in HMPA[8] readily gave **10**.

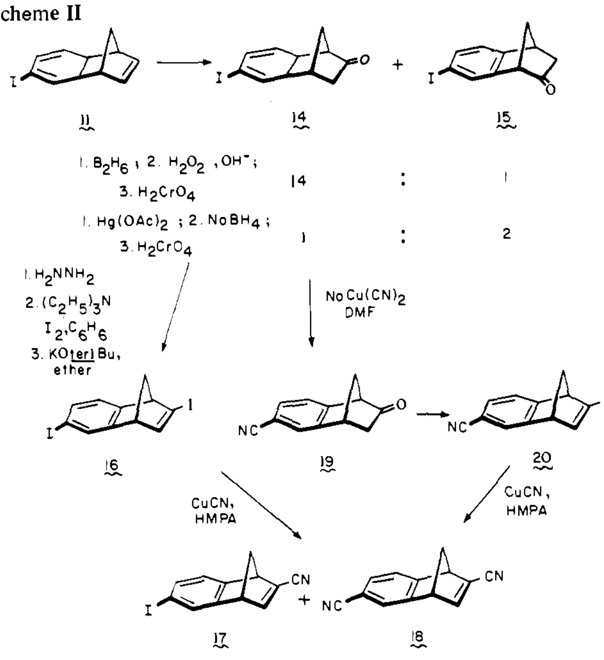
With the availability of 6-iodobenzonorbornadiene (**11**),[3] our attention was next directed to methods for the functionalization of its double bond. The pair of mechanistic options available to **11** during its involvement in electrophilic addition



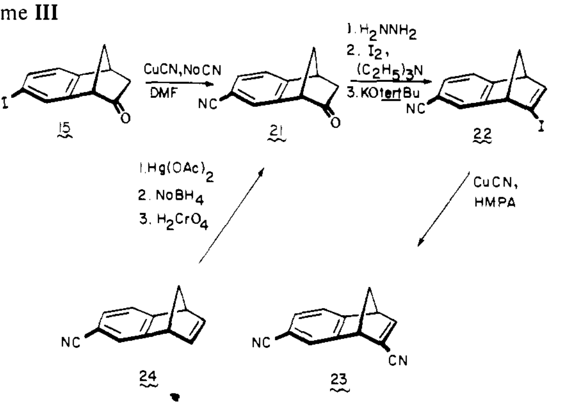
reactions consist of homo-meta (**12**) or homo-para cation (**13**) formation. Owing to the substantial aryl $p\pi$ participation during solvolysis of 2-benzonorbornenyl derivatives[9–12] and the very significant effects of 6- and 7-substituents on reaction rates,[10] the expectation was that the homo-para carbocation would be less energetically favored in this instance. This conclusion was derived principally from the opposite sign of the σ^* values determined for *p*-I (+0.135) and *p*-OCH$_3$ (−0.778),[13] the previously substantiated stabilization by 6-OCH$_3$ of the homo-para cation,[9c,10b,11a,c] and the known opposite influence of 6-F.[14]

As shown in Scheme II, the enhanced electronic stabilization of **12** can be used to synthetic advantage. While the hydroboration-oxidation approach provided a 14:1 mixture of ketones **14** and **15**, oxymercuration–demercuration and subsequent Jones oxidation gave rise to **15** as the major product. In agreement with these assignments, the characteristic ^1L_a bands

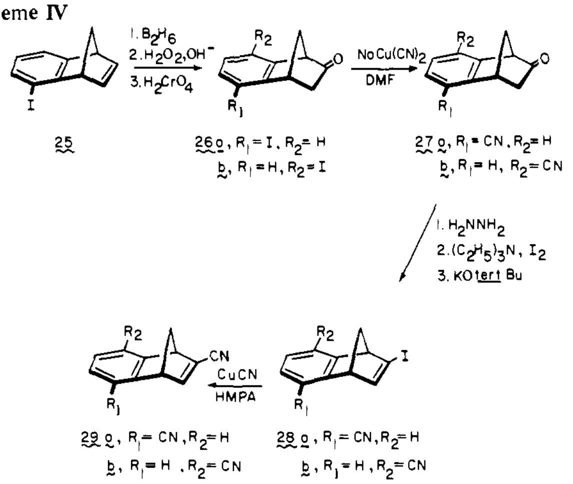
Scheme II



Scheme III



Scheme IV



in the ultraviolet spectra of **14** and **15** (isooctane solution) appeared at 237.5 (ϵ 20 700) and 240 nm (18 200), respectively.[15] Although the gap between these maxima is not as large as in the corresponding methoxy ketones,[10c] the more powerful electron-withdrawing effect of the iodine in **14** is quite apparent.

Starting with **14**, conversion to diiodide **16** proceeded only in low (20%) yield. Additionally, subsequent halogen displacement by cyanide was not clean. A mixture of **17** and the desired **18** was invariably obtained, with the attendant need for preparative thick-layer chromatographic separation. On the other hand, direct cyanation of **14** and the subsequent elaboration of **21** could be achieved without complication. Since 2,6-dicyanobenzonorbornadiene (**18**) was subsequently formed in good yield from **20**, this approach was utilized to prepare the remaining three isomers (Schemes III and IV).

The uniform success of this route can be traced to the efficacious introduction of cyano when iodo ketones **14**, **15**, and **26** were treated with sodium dicyanocuprate in hot dimethylformamide.[15] This is likely due to the heightened reactivity of these ketones, the enhanced solubility of the complex, and the resultant homogeneity of the reaction mixture.

Additional confirmation of the structural assignment to **21** was gained by oxymercuration–demercuration and oxidation of 6-cyanobenzonorbornadiene (**24**). In this example, strong homo-meta orientation of the developing positive charge is expected. Capture of nucleophilic water at this site would ultimately deliver **21** as was observed.

Of comparable critical importance is a clear-cut distinction between ketones **26a** and **26b** which are obtained in a 1:4 ratio upon hydroboration–oxidation of **25** under dilute conditions. For some unexplained reason, the relative amounts of these iodo ketones became more equitable (1:1.5) when the reaction mixture was made more concentrated. With mercuric acetate as the reagent, **26a** was seen to be the dominant product. For electronic reasons similar to those discussed previously, the

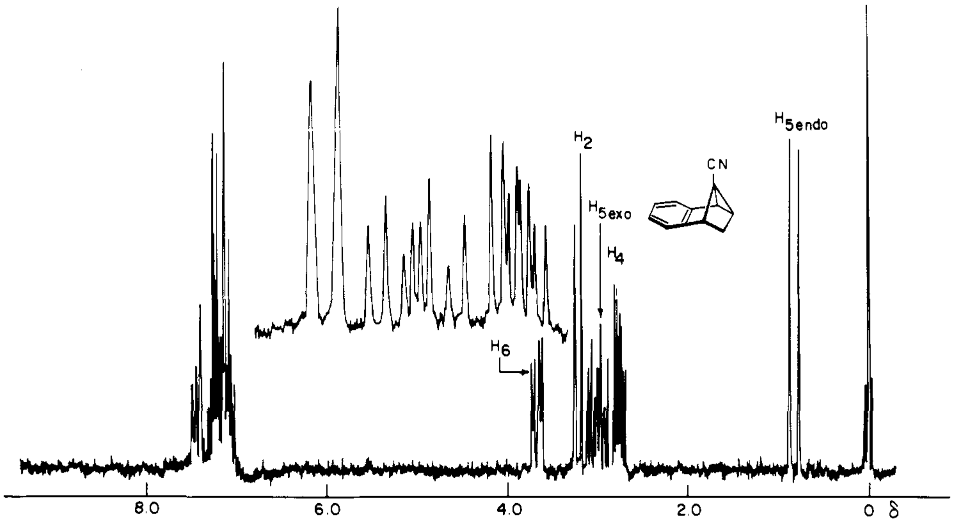


Figure 1. ^{1}H NMR spectrum (90 MHz, CDCl$_3$ solution) of **30**.

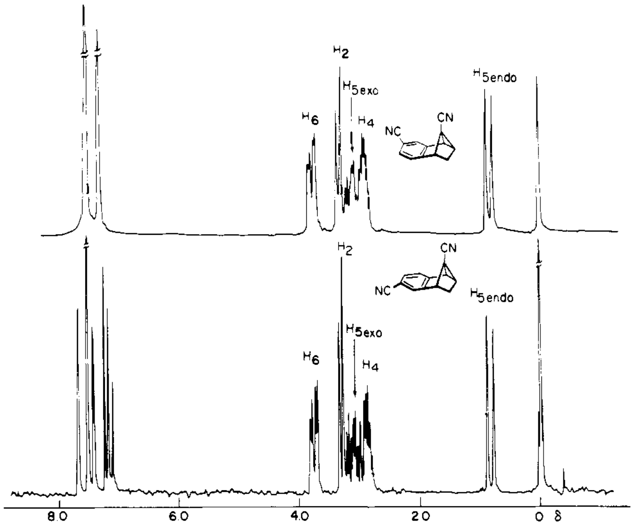


Figure 2. ^{1}H NMR spectra (90 MHz, CDCl$_3$ solution) of **31a** (top) and **31b** (bottom).

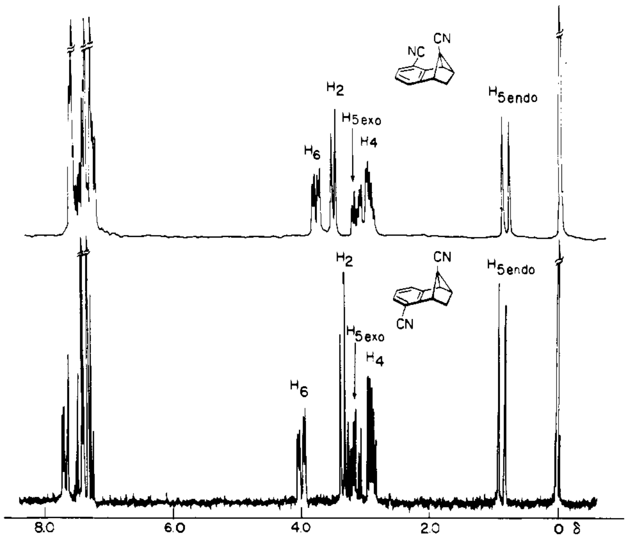
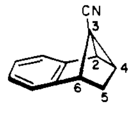


Figure 3. ^{1}H NMR spectra (90 MHz, CDCl$_3$ solution) of **32b** (top) and **32a** (bottom).

homo-ortho cation derived from **25** should be disfavored relative to its homo-meta counterpart. Although it is difficult to prove the structures of **27a** and **27b** unambiguously without making recourse to crystal structure analysis, the weight of evidence derived from the excited state behavior of dinitriles **29a** and **29b** and particularly the 2-methyl substituted derivatives (**28**, I = CH$_3$)[17] is convincing.

Photoisomerization Studies. The photolysis of **10** was examined first. As in our subsequent study of the dicyanobenzonorbornadienes, irradiation was conducted in benzene solution containing acetophenone as sensitizer with a bank of 3500-Å lamps in a Rayonet reactor. Isomerization was seen to be very rapid, high yield conversion to a single tetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene being complete in 20–40 min. The aliphatic region of the 90-MHz ^{1}H NMR spectrum of the photoproduct in CDCl$_3$, which is illustrated in Figure 1, is seen to be divided into five distinct regions which uniquely characterize each relevant proton. That the cyano group must be positioned at C$_3$ follows unequivocally from several observations: (a) the spectra of a large collection of tetracyclo[5.4.0.0^{2,4}.0^{3,6}]undecatrienes which are unsubstituted in the alicyclic moiety show that H$_3$ and H$_6$ almost invariably appear as two overlapping multiplets at low field; in the present example, there is but a doublet of doublets in this region (δ 3.69) and therefore one of these protons is clearly lacking; (b) the multiplicity and coupling constants of the low field absorption (7.5 and 2.8 Hz) conform to those anticipated for $J_{5\text{exo},6}$ and $J_{4,6}$, respectively, but not to those customarily observed for H$_3$; (c) the H$_{5\text{endo}}$ proton, which is heavily shielded because of its proximity to the arene π cloud, appears at δ 0.82 as a doublet (J = 9.5 Hz) due to its large spin interaction with H$_{5\text{exo}}$; earlier observations indicate that the presence of H$_3$ would introduce additional coupling to H$_{5\text{endo}}$ as a result of their W-plan arrangement; (d) appropriate simplification of the remaining signals in line with the absence of H$_3$ (but not H$_6$); (e) the unquestionable presence of H$_2$, the anticipated site of cyano substitution if the alternate di-π-methane rearrangement pathway had materialized. Accordingly, this information establishes **30** as the regioisomer which has been formed.



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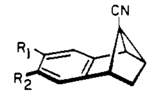
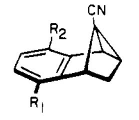


31 **a**, R$_1$ = CN, R$_2$ = H
b, R$_1$ = H, R$_2$ = CN



32 **a**, R$_1$ = CN, R$_2$ = H
b, R$_1$ = H, R$_2$ = CN

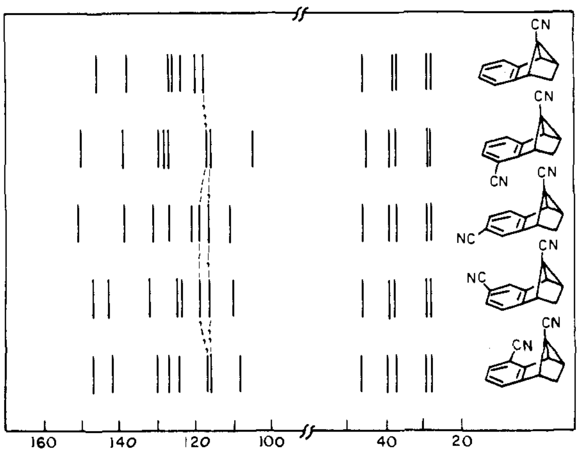


Figure 4. Schematic bar graph of the ^{13}C chemical shifts in the cyano-substituted tetracyclo[5.4.0.$0^{2,4}$.$0^{3,6}$]undeca-1(7),8,10-trienes. The vertical dotted lines interconnect the signals attributable to the nitrile carbon atoms.

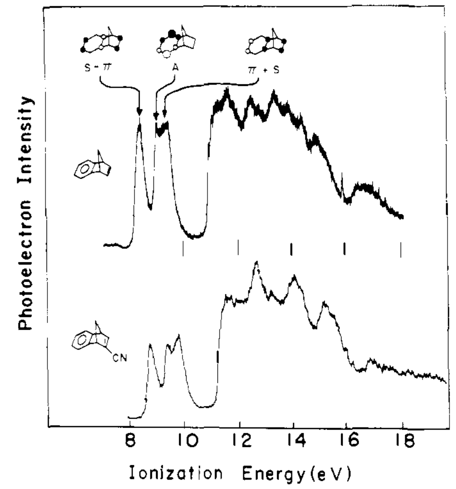


Figure 5. Photoelectron spectra of **1** and **10**. The π orbitals giving rise to the first three ionizations are sketched at the top of the drawing.

It was subsequently found that the triplet excited state photorearrangements of the dicyanobenzonorbornadienes were equally regiospecific within the limits of detectability (TLC and ^1H NMR analysis). Thus, **18** and **23** proved to be the progenitors of **31a** and **31b**, respectively, while **29a** and **29b** gave rise in turn to **32b** and **32a**. To facilitate comparison of the structural relationship of the photoproducts, their 90-MHz ^1H NMR spectra are illustrated in Figures 2 and 3. In each instance, conversion to the tetracyclo[5.4.0.$0^{2,4}$.$0^{3,6}$]undecatriene carrying a cyano substituent at C_3 was observed to occur with ease and in high chemical yield, irrespective of the locus of the aryl-CN group. Since the set of four photolysis experiments provided all of the possible aryl substitution plans in the 3-cyano series without mutual intercontamination, the question of possible thermodynamic control by the aryl cyano group of the photoisomerization can be discounted. Also, reactions conducted to 10–20% conversion gave no indication of the presence of 2-cyano isomers. On this basis, it would appear that the regiospecificity is the direct result of kinetic factors operating during the bond-making process (see Discussion).

Further evidence for the identity of the assigned photoproduct structures in all five systems can be gained from examination of the ^{13}C NMR spectra (Figure 4). While the chemical shifts of the saturated carbons are characterized by a striking near identity, the trigonal carbon atoms of the aromatic ring reflect the changes brought about by positioning the second cyano sequentially at C_8 to C_{11}.

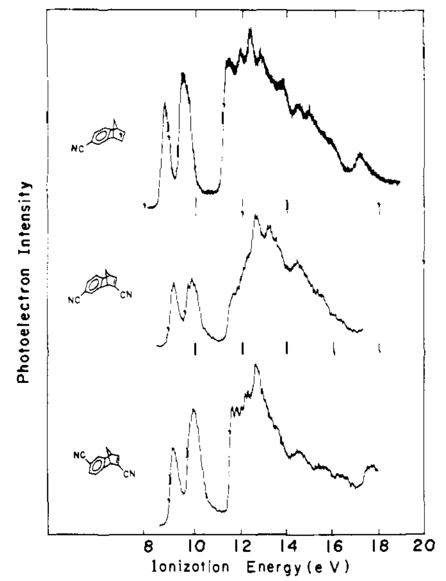


Figure 6. Photoelectron spectra of "*meta*"-cyano (6-cyano-, 2,6-dicyano-, 2,7-dicyano-) benzonorbornadienes.

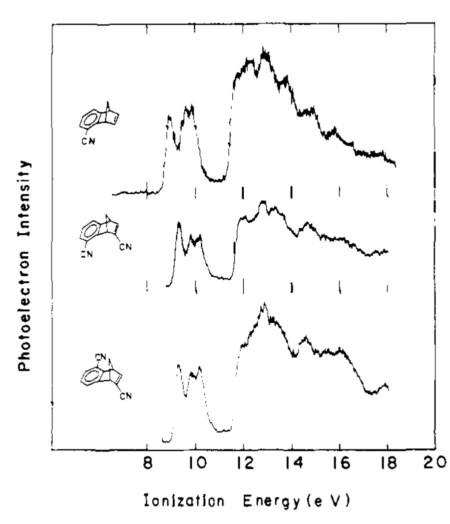


Figure 7. Photoelectron spectra of "*ortho*"-cyano (5-cyano, 2,5-dicyano-, 2,8-dicyano-) benzonorbornadienes.

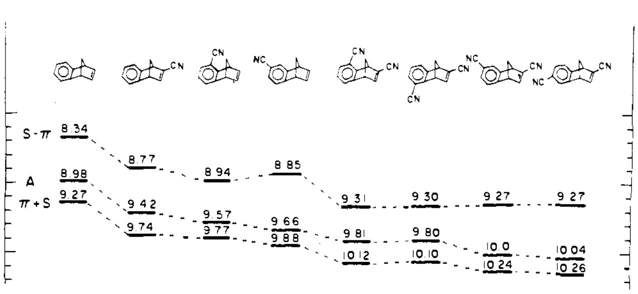


Figure 8. Correlations between π ionization potentials of the mono- and dicyanobenzonorbornadienes.

Photoelectron Spectroscopic Analysis. With investigation of the reaction regiochemistry completed, the ionization potentials of the cyano substituted benzonorbornadienes were next elucidated by means of photoelectron spectroscopy. The spectra are shown in Figures 5–7, and the ionization potentials are tabulated in Figure 8. Remarkably, the spectra of the parent benzonorbornadiene (**1**)[18] and its 2-cyano derivative (**10**) are closely similar, except that all ionization potentials

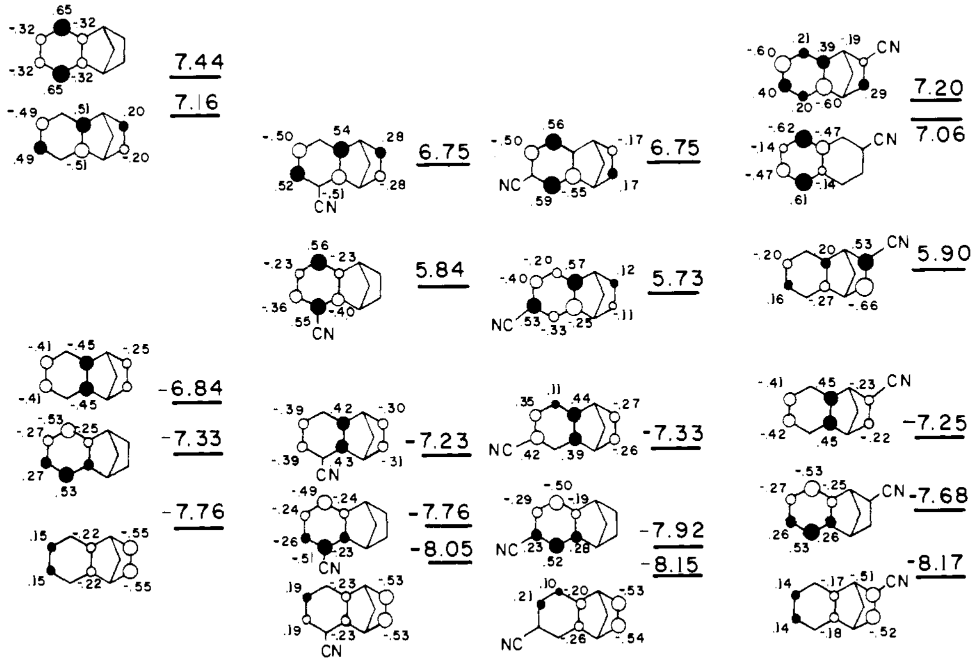


Figure 9. STO-3G orbital energies and shapes for cyanobenzonorbornadienes.

of **10** are about 0.45 eV higher than those of the hydrocarbon (Figures 5 and 8). There are some additional maxima in the 12-14-eV region of the 2-cyanobenzonorbornadiene spectrum due to π_{CN} and n_N orbitals which appear at about 12 and 13 eV, respectively, as in acrylonitrile and other alkenyl nitriles.[19] As will be discussed in more detail elsewhere, the cyano group has a rather nonspecific effect on the various π and σ ionization potentials, raising all of these to a similar extent.[20] That is, regardless of the localization of the positive charge in the various radical cation states, all are destabilized to a similar extent by the cyano group. Of particular note, the second IP of benzonorbornadiene, which arises from an orbital which is completely localized on the aromatic ring (Figure 5), is influenced by cyano substitution nearly as much as the first and third IP's, which both arise from orbitals with substantial density on the vinyl carbons. The photoelectron spectra of the dicyanobenzonorbornadienes also reflect this phenomenon (Figures 6 and 7). The first three ionization potentials are all raised by 0.45 ± 0.02 eV relative to **10**, but since experimental error is about ±0.05 eV and the broad shapes of the bands make accurate assignment of the vertical IP's uncertain, we may say that all three π IP's in **18, 23, 29a,** and **29b** are displaced by 0.45 ± 0.1 eV. As described in the next section, the shapes of occupied orbitals are charged to a very small extent by cyano substitution.

The spectra of 5- and 6-cyanobenzonorbornadiene are very similar to that of the 2-cyano derivative. For these three molecules, the first IP's are 8.85 ± 0.09, 9.55 ± 0.13, and 9.80 ± 0.08 eV. Due to uncertainties mentioned above, only the second IP's are significantly different from each other, with the aryl cyano compounds having higher second IP's than the vinyl cyano. In spite of the fact that the first and third IP's of benzonorbornadiene arise from orbitals having a node at C-5, a 5-cyano substituent influences these IP's nearly as much as a 6-cyano substituent.

The spectra of the dicyano compounds are shown along with the appropriate aryl monocyano compound in Figures 6 and 7. The addition of a second cyano group to *o*-cyanobenzonorbornadiene at either the 2- or 3- (vinyl) position causes a somewhat larger increase in the first and third IP's than in the second. The spectra of 2,5- and 2,8-dicyanobenzonorbornadiene are virtually indistinguishable in the low IP region of the spectrum.

Similarly, conversion of the meta compound to the dicyano substituted systems causes an increase in all three IP's of 0.38 ± 0.04 eV and the 2,6- and 2,7-dicyanobenzonorbornadienes have very similar spectra.

While we defer more detailed discussion of this unusual effect of cyano substitution,[20] we tentatively conclude that the cyano group is withdrawing electron density more or less uniformly from all regions of the molecule. This is very different from the usual concept of inductive or field effects, which fall off rapidly with distance.

STO-3G Calculations on Cyanobenzonorbornadienes. Figure 9 summarizes the result of ab initio STO-3G[21] calculations on benzonorbornadiene and three cyanobenzonorbornadienes.[22] The calculations provide information on how the orbital shapes are influenced by cyano substitution at various positions. For the occupied orbitals, the cyano group energy-lowering effect is felt in all orbitals, and is not simply related to the shape of the orbital. For example, the 2-cyano substituent lowers the second highest occupied orbital (SHOMO) nearly as much as the highest and third highest occupied orbitals, in spite of the fact that the SHOMO is entirely localized on the aromatic moiety. The mechanism of the cyano group substituent effect can be threefold. First, there can be an "inductive" effect, which may consist of both σ electron withdrawal and polarization, and a field component. That is, partial removal of an electron from the σ skeleton, or simply bringing a positive charge into the vicinity of the molecule, will lower orbital energies, or increase IP's, by increasing the attraction of an electron for the nuclei or positively charged moiety, respectively. Secondly, the cyano group can act as a "resonance" or π-electron withdrawer or polarizer through its low-lying vacant π^*_{CN} orbital. Thirdly, the cyano can be a "resonance" or π donor and polarizer by virtue of the presence of its filled π_{CN} orbital.[23]

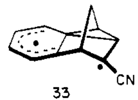
The rather unspecific effect of cyano on the orbital energies and IP's speaks for an inductive effect, which, however, does not fall off rapidly with distance, but makes all IP's, regardless of localization of the corresponding orbitals, higher. The relatively minor changes in the occupied orbital shapes also suggests this mechanism.

By contrast, the vacant orbitals are changed in shape and energy quite specifically by the cyano. In addition to the large nonspecific energy lowering felt in both filled and vacant orbitals, substantial mixing of the π^*_{CN} orbitals with the vacant benzonorbornadiene orbitals occurs, and the larger the coefficient at the site of substitution, the greater the resultant mixing. Thus, cyano groups influence vacant orbital energies and shapes most when attached at the site of a large coefficient.

Discussion

Nature of the Regiospecificity. As a direct consequence of the reaction conditions employed (acetophenone sensitization), the triplet states of the variously substituted benzonorbornadienes are implicated as the entities which initiate photorearrangement. Substantial earlier precedent also lends strong credence to this prevailing state of affairs.[24] The most striking result, however, is the complete regiospecificity of the several photoisomerizations, irrespective of the location of the powerful electron-withdrawing aryl cyano substituent. In view of the excited state behavior of **10** which undergoes electronic reorganization with benzo-vinyl bridging to give exclusively **33**, it is quite apparent that the vinyl cyano substituent exerts a meaningful stabilizing effect on the biradical intermediate when the aromatic ring is unsubstituted.

A similar controlling influence has been noted by Bender and co-workers during the triplet sensitized photolysis of 2-cyanobenzobarrelene (**34**).[25] By means of the indicated deuterium labeling scheme, it was possible to establish that di-π-methane rearrangement was initiated by regiospecific vinyl-vinyl bridging to give **35**, the precursor to **36**. In direct irradiation experiments, **34** gave benzocyclooctatetraenes **37** (65%) and **38** (35%) by vinyl-vinyl and benzo-vinyl bridging, respectively.[25a] In contrast, the parent benzobarrelene hydrocarbon which lacks the polar substituent is subject only to benzo-vinyl bridging under the same conditions.[26] Thus, the control of regiochemistry by the cyano group is made manifest to the higher degree in triplet state processes.



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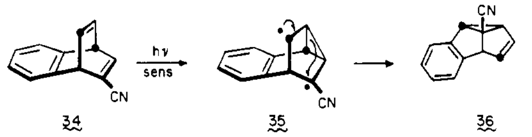
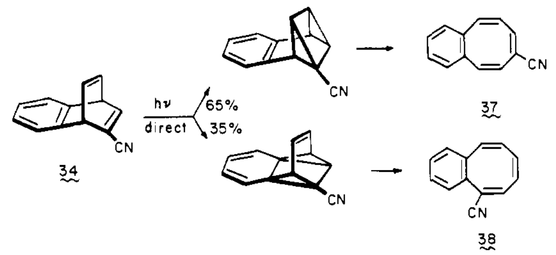
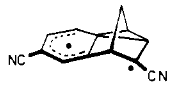




The intervention of **33**, anticipated from earlier theoretical considerations,[5] is presumably further intensified in the triplet excited states derived from **23** and **29a**. As seen in formulas **39** and **40**, the bonding processes which place an odd electron α to vinyl cyano is fostered additionally by the inherent bridging tendency of meta CN (para-bonding)[3] and ortho CN (ortho bonding).[4] Because these effects are additive, the photorearrangements of **23** and **29a** should also give rise to only one product, and they do.



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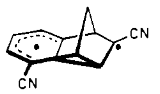
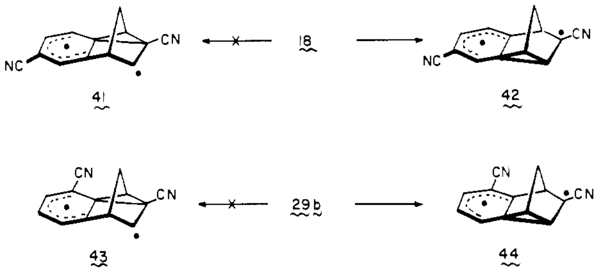


40

However, this pair of experiments does not provide important insight into the relative efficacies of competitive aryl-vinyl bridging which is made available by their isomers **18** and **29b**. In evaluating the two di-π-methane options available to **18**, one sees that the reaction course which would operate under control of the aryl cyano group would deliver **41** by para-bridging and receive no obvious stabilization from aliphatic cyano which finds itself bonded to a cyclopropane ring. Alternatively, domination by vinyl cyano would result in formation of biradical **42** where unfavorable meta-bridging is forced upon the polar aryl substituent. Analogous perturbations are at play during the potential conversion of **29b** to **43** and **44**. Our results show that only **42** and **44** intervene and therefore that electron spin density in this pair of intermediates prefers to be concentrated at C_2, α to the original vinyl cyano substituent.



At this point, it becomes important to reemphasize that di-π-methane rearrangements are two-step processes and that only the overall chemical result is directly observable. The bridging step probably requires some activation energy to be surmounted because of the loss of benzenoid character, while the bond-breaking should have little, if any, energy demands. Accordingly, biradical formation is considered to be the porduct-determining step. However, it becomes necessary to assume that biradicals **41** and **43** do not experience triplet decay more rapidly than **42** and **44**, respectively. Once ground state biradicals are produced, return to starting material would occur.[27] Such eventualities appear unlikely, since the acceptor groups in **42** and **44** are best oriented to interact with an odd electron and facilitate spin inversion; regiospecificity opposite to that which is observed would then result. Although quantum yield measurements would *at first glance* appear capable of shedding additional light on these questions, it must be kept in mind that relative quantum yields, especially for triplet reactions, often are completely unrelated to relative rate constants for excited state reactions.[28] Such studies have therefore not been performed. To sum up, however, we regard the relative rates of benzo-vinyl bridging to be the source of the regiospecificity.

Photochemical Rearrangements and Orbital Shapes. While the conversions of **18** to **42** and of **29b** to **44** signal a greater capability of vinyl cyano to stabilize transition states relative to aryl cyano, regardless of its bonding location, it is likely that more deep-seated donor-acceptor interactions contribute significantly to the exclusivety of these reaction channels.

We have shown earlier that the vacant orbital energies and shapes dominate bridging regioselectivity in benzonorbornadienes substituted on the aromatic ring by acceptor substituents.[18] In the case of the monocyano compounds, the LUMO polarization by the 2-cyano substituent in **10** is large, but not much larger than that caused by 5- or 6-cyano substitution (Figure 9). However, the excited triplet state can only be described as a combination of two or more configurations, and the aromatic portion of the LUMO and SLUMO are polarized in an opposite fashion. That is, cyano substitution on the aromatic ring does favor ortho (5) or para (6) bridging, but the effect is not nearly as large as the effect of cyano at the 2-

position, which favors only 3-bridging in all orbitals to which $\pi^*_{2,3}$ contributes. Furthermore, the 2-cyano group drastically lowers the energy of the orbital which is mainly $\pi^*_{2,3}$ in character from 8.7 eV in the unsubstituted compound to 5.9 eV in the 2-cyano compound. Thus, whereas the lowest excited triplet of benzonorbornadiene (**1**) is basically a slightly perturbed aromatic transition, that of the 2-cyano compounds should have considerably more aromatic-to-vinyl charge-transfer character. Although calculations were not carried out on the dicyano compounds, the LUMO's of these compounds should be relatively heavily concentrated on the C-2, C-3 bond, and should be polarized in the same fashion as the LUMO shown in Figure 9 for 2-cyanobenzonorbornadiene.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^{1}H NMR spectra were determined with Varian T-60, Varian A-60A, and Bruker HX-90 instruments, and apparent splittings are given in all cases. The ^{13}C spectra were also obtained with the Bruker spectrometer. Mass spectra were measured on an AEI-MS9 spectrometer at an ionizing energy of 70 eV. The photoelectron spectra were recorded on a Perkin-Elmer PS-18 photoelectron spectrometer using xenon and argon as calibrants. The instrumental resolution was approximately 20 meV for all spectra recorded herein. Preparative scale VPC separations were performed on Varian Aerograph Model A-90-P3 instruments equipped with thermal conductivity detectors. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

2-Cyanobenzonorbornadiene (10). A solution of benzonorbornen-2-one (**8**)[29] (6.0 g, 35.7 mmol), hydrazine hydrate (17.9 g, 0.36 mol), and triethylamine (54.2 g, 0.536 mol) in ethanol (60 mL) was refluxed for 2 h. Hot water was added slowly until the solution became cloudy. The mixture was allowed to cool and set in a freezer overnight. Extraction with ether (3 × 75 mL), followed by drying of the combined organic phases and solvent evaporation, left 6.1 g (99%) of the clear, oily hydrazone.

The hydrazone (6.0 g, 34.8 mmol) in dry benzene (70 mL) containing triethylamine (35.2 g, 0.35 mol) was treated slowly with iodine (17.7 g, 69.6 mmol) in benzene (50 mL) under a nitrogen atmosphere. Upon completion of the addition, the mixture was allowed to stand at room temperature for 1 h, then poured into water. The aqueous phase was extracted with ether and the combined organic layers were shaken with 2 N hydrochloric acid, water, 10% sodium bisulfite solution, water, saturated sodium bicarbonate solution, and water before drying. Upon removal of the solvent under reduced pressure, the residual oil was shown to be chiefly *gem*-diiodide by NMR spectroscopy. This material was taken up in hydrous ether (50 mL) and treated portionwise with solid potassium *tert*-butoxide (5.86 g, 52.2 mmol) with stirring at 0 °C. After 12 h, water was added, the ether layer was separated and dried, and the solvent was evaporated. The residual oil was distilled and the fraction boiling at 72-75 °C (0.1 mm) was chromatographed on silica gel (hexane elution) to give 4.4 g (47%) of **9** which was utilized without further purification: ^{1}H NMR (δ, $CDCl_3$) 7.3-6.8 (m, 5 H), 3.83 (m, 2 H), and 2.65-2.0 (m, 2 H); *m/e* calcd 267.9751, obsd 267.9759.

The iodide in HMPA (75 mL) containing cuprous cyanide (3.67 g, 41.0 mmol) was heated at 90-95 °C for 3 h under nitrogen, cooled, and poured into aqueous ferric chloride solution to decompose the complex. The resulting brown oil which separated was chromatographed on silica gel. Elution with pentane removed a byproduct, while elution with 40% ether in pentane afforded **10** as a colorless oil which crystallized on standing in the cold (1.40 g, 51%). Repeated sublimation gave the analytical sample, mp 38-39 °C: ν_{max}^{KBr} 2205 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 7.5-6.8 (series of m, 5 H), 4.10 (m, 2 H), and 3.65-2.2 (m, 2 H); *m/e* calcd 167.0735, obsd 167.0739.

Anal. Calcd for $C_{12}H_9N$: C, 86.19; H, 5.43. Found: C, 86.10; H, 5.51.

Hydroboration-Oxidation of 6-Iodobenzonorbornadiene (11). A 6.0-g (22.4 mmol) sample of **11**[3] in ice-cold dry tetrahydrofuran (75 mL) was treated with excess diborane introduced in a nitrogen stream. Upon completion of the addition, the mixture was heated at reflux for 2 h, cooled to 0 °C, and treated sequentially with ice chips, 1.5 equiv of 3 N sodium hydroxide solution, and 1.5 equiv of 30% hydrogen peroxide solution at 0 °C. The resultant solution was stirred for 2 h at room temperature, diluted with ether, washed with water, and dried. Solvent removal left a colorless oil which was directly subjected to Jones oxidation. The isomeric ketones (4.8 g, 75%) could be separated by chromatography on silica gel (elution with 10% ethyl acetate in hexane). The first compound to elute was minor component **15** which proved identical with the major oxymercuration product (characterized below). The major component (**14**) was recrystallized from methanol and sublimed to give colorless crystals, mp 87-88.5 °C; ν_{max}^{KBr} 1740 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 7.57-6.9 (m, 3 H), 3.7-3.45 (m, 2 H), and 2.65-1.9 (m, 4 H); ^{13}C NMR (ppm, $CDCl_3$) 212.10, 148.26, 142.37, 136.36, 132.48, 123.56, 91.33, 57.77, 50.67, 41.57, and 39.87; *m/e* 284 (M$^+$); $\lambda_{max}^{isooctane}$ 237.5 (ϵ 20 700), 244 (17 700), 300 (1850), 311 (1710), and 322.5 nm (570).

Anal. Calcd for $C_{11}H_9IO$: C, 46.48; H, 3.20. Found: C, 46.87; H, 3.18.

Oxymercuration-Oxidation of 6-Iodobenzonorbornadiene (11). To a cold (0 °C) solution of mercuric acetate (23.8 g, 74.6 mmol) in water (75 mL) and tetrahydrofuran (75 mL) was added 2.0 g (7.46 mmol) of **11**. After the mixture was stirred at room temperature for 2 h, 70 mL of 3 M sodium hydroxide solution was introduced dropwise at 0 °C followed by 70 mL of 0.5 M sodium borohydride in 3 M NaOH. The liberated elemental mercury was allowed to settle, solid sodium chloride was added to saturate the aqueous phase, and the upper tetrahydrofuran layer was separated and taken into ether. The ethereal solution was washed with water, dried, and evaporated. The resultant colorless oil was subjected to Jones oxidation to give a mixture of **14** and **15** (1.5 g, 71%, ratio 1:2) which was separated by medium-pressure liquid chromatography. Pure **15** (1.0 g isolated) was obtained from methanol as colorless prisms, mp 57-58 °C; ν_{max}^{KBr} 1740 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 7.65-6.9 (m, 3 H), 3.7-3.45 (m, 2 H), and 2.6-1.7 (br m, 4 H); ^{13}C NMR (ppm, $CDCl_3$) 122.04, 150.99, 139.58, 135.82, 130.84, 125.38, 92.55, 57.71, 50.61, 41.69, and 39.87; *m/e* 284 (M$^+$); $\lambda_{max}^{isooctane}$ 240 (ϵ 18 200), 246 (20 800), 298 (1850), 309 (1710), and 321.5 nm (570).

Anal. Calcd for $C_{11}H_9IO$: C, 46.48; H, 3.20. Found: C, 46.48; H, 3.19.

2,6-Diiodobenzonorbornadiene (16). Treatment of 500 mg of **14** with hydrazine hydrate as above afforded the hydrazone in 95% yield. Subsequent conversion to **16** as outlined gave 139 mg (20%) of **16:** ^{1}H NMR (δ, $CDCl_3$) 7.43-6.9 (m, 4 H), 3.76 (m, 2 H), and 2.46-1.85 (m, 2 H); *m/e* 393 (M$^+$).

2-Cyano-6-iodobenzonorbornadiene (17). To a solution of **16** (100 mg, 0.25 mmol) in hexamethylphosphoric triamide was added 60 mg (0.67 mmol) of cuprous cyanide and the mixture was heated at 90-95 °C for 3 h. The predescribed workup gave an impure product which was purified by preparative thick-layer chromatography on silica gel (elution with 15% ethyl acetate in hexane). There were isolated 30 mg (40%) of **17** and 15 mg (31%) of **18.** For **17:** mp 63-64 °C; ν_{max}^{KBr} 2210 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 7.53-6.93 (m, 4 H), 4.03 (m, 2 H), and 2.40 (m, 2 H); *m/e* calcd 292.9703, obsd 292.9710.

6-Cyanobenzonorbornen-2-one (19). A 2.0-g (7.0 mmol) sample of **14** dissolved in dry dimethylformamide was treated with 0.86 g (17.5 mmol) of sodium cyanide and 1.57 g (17.5 mmol) of cuprous cyanide and refluxed for 4 h. The cooled reaction mixture was poured into a saturated aqueous sodium cyanide solution and ether was added. The slurry was stirred for 30 min, the ether layer was separated, and the aqueous phase was entracted with ether. The combined ethereal solutions were washed well with water, dried, and evaporated to give 1.0 g (78%) of **19.** Recrystallization from methanol and sublimation furnished colorless crystals, mp 115-116 °C; ν_{max}^{KBr} 2210 and 1750 cm^{-1}; ^{1}H NMR (δ, C_6D_6) 7.28-6.35 (m, 3 H), 3.02 (narrow m, 1 H), 2.80 (m, 1 H), and 1.95-1.15 (m, 4 H); ^{13}C NMR (ppm, $CDCl_3$) 210.82, 153.78, 141.34, 132.24, 136.59, 122.40, 118.76, 110.69, 57.71, 50.61, 42.12, and 39.32; $\lambda_{max}^{isooctane}$ 241 (ϵ 11 200), 249 (11 200), 299 (830), 310 (750), and 322 nm (455); *m/e* calcd 183.0684, obsd 183.0688.

Anal. Calcd for $C_{12}H_9NO$: C, 78.67; H, 4.95. Found: C, 78.47; H, 5.15.

2-Iodo-6-cyanobenzonorbornadiene (20). Conversion of **19** (800 mg, 4.37 mmol) to its hydrazone proceeded quantitatively. Treatment of this derivative in cold (0 °C) benzene solution (25 mL) containing triethylamine (10 mL) with a solution of iodine (2.5 g) in benzene (25 mL) afforded chiefly the *gem*-diiodo compound. The latter was stirred in ether with 75 mg of potassium *tert* butoxide for 45 min. Workup and silica gel chromatography furnished a yellowish oil, crystallization of which from ether and hexane gave 370 mg (29%) of **20** as a colorless solid, mp 67–68.5 °C ^{1}H NMR (δ, $CDCl_3$) 7.43–6.85 (m, 4 H), 3.9 (m, 2 H), 2.52 (dt, *J* = 7.5 and 1 Hz, 1 H), and 2.18 (dt, *J* = 7.5 and 1 Hz, 1 H); *m/e* calcd 292.9703, obsd 292.9710.

2,6-Dicyanobenzonorbornadiene (18). Vinyl iodide **20** (185 mg, 0.63 mmol) was heated with excess cuprous cyanide in HMPA in the manner described above. The dinitrile so produced (101 mg, 83%) was recrystallized from methanol and obtained as colorless crystals, mp 117–118 °C: ν_{max}^{KBr} 2210 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 7.52 (narrow m, 2 H), 7.3 (pseudo s, 2 H), 4.16 (narrow m, 2 H), and 2.68–2.2 (m, 2 H); ^{13}C NMR (ppm, $CDCl_3$) 158.37, 153.37, 149.87, 131.13, 127.88, 125.45, 123.36, 118.90, 115.30, 109.53, 69.81, 53.06, and 51.85; *m/e* calcd 192.0687, obsd 192.0691.

Anal. Calcd for $C_{13}H_8N_2$: C, 81.22; H, 4.20. Found: C, 81.04; H, 4.22.

7-Cyanobenzonorbornene-2-one (21). (A) Cyanation of 15. Treatment of **15** (3.0 g, 10.6 mmol) with sodium dicyanocuprate as previously detailed provided 1.51 g (78%) of **21** as a colorless solid, mp 90–91 °C (from methanol): ν_{max}^{KBr} 2215 and 1750 cm^{-1}; ^{1}H NMR (δ, C_6D_6) 6.9–6.35 (m, 3 H), 3.03 (m, 1 H), 2.72 (m, 1 H), and 2.0–1.05 (br m, 4 H); $\lambda_{max}^{isooctane}$ 241.5 (ϵ 13 900), 248 (14 060), 300 (1210). 310.5 (910), and 323 nm (300): *m/e* calcd 183.0684, obsd 183.0690.

Anal. Calcd for $C_{12}H_9NO$: C, 78.66; H, 4.95. Found: C, 78.82; H, 5.08.

(B) Oxymercuration–Oxidation of 6-Cyanobenzonorbornadiene (24). Reaction of **24**[3] (120 mg, 0.72 mmol) with mercuric acetate in the predescribed manner followed by Jones oxidation and recrystallization of the crude product from methanol gave 40 mg (30.5%) of **21**, mp 88–90 °C (from ether–petroleum ether). This ketone proved identical in all respects to the sample prepared by procedure A.

2,7-Dicyanobenzonorbornadiene (23). The hydrazone of **21,** obtained from 3.0 g (16.4 mmol) of the ketone in quantitative yield, was converted without purification to vinyl iodide **22** (47%): ^{1}H NMR (δ, $CDCl_3$) 7.5–6.93 (m, 4 H), 3.96 (m, 2 H), and 2.7–1.9 (br m, 2 H). There was obtained 1.5 g (37%) of unpurified product, 1.2 g of which was treated with cuprous cyanide in HMPA at 90–95 °C as before. The resulting dinitrile was purified by silica gel chromatography and sublimation (50 °C, 0.01 mm), colorless crystals, mp 94–95 °C: ^{1}H NMR (δ, $CDCl_3$) 7.6–7.2 (m, 4 H), 4.16 (m, 2 H), and 2.6–2.1 (m, 2 H); ^{13}C NMR (ppm, $CDCl_3$) 158.71, 154.09, 149.09, 130.94, 127.59, 125.60, 123.22, 118.90, 115.52, 109.82, 69.72, 53.50, and 51.41; *m/e* calcd 192.0687, obsd 192.0691.

Anal Calcd for $C_{13}H_8N_2$: C, 81.22; H, 4.20. Found: C, 81.00; H, 4.25.

5-Iodobenzonorbornen-2-one (26a) and 8-Iodobenzonorbornen-2-one (26b). A 500-mg (1.86 mmol) sample of 5-iodobenzonorbornadiene (**25**)[4] was subjected to sequential hydroboration and Jones oxidation according to the usual procedure. The product was chromatographed on silica gel (10% ethyl acetate in hexane as eluent) to give 330 mg (58%) of **26b** and 80 mg (14%) of **26a.** When this reaction sequence was conducted on a larger scale in more concentrated solution, the ratio of ketones differed. Thus, 15 g of **25** was converted to 7.5 g of **26b** and 5 g of **26a** (78.7% total yield).

Ketone **26a,** colorless crystals, mp 56–57 °C: ν_{max}^{KBr} 1750 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 7.45 (dd, *J* = 8 and 1 Hz, 1 H), 7.18 (dd, *J* = 8 and 1 Hz, 1 H), 6.86 (d, *J* = 8 Hz, 1 H), 3.7 (m, 2 H), and 2.6–2.0 (br m, 4 H); ^{13}C NMR (ppm, $CDCl_3$) 212.10, 140.97, 136.48, 128.72, 123.13, 89.51, 59.53, 49.64, 46.12, and 28.90; *m/e* calcd 382.9700, obsd 283.9707.

Anal. Calcd for $C_{11}H_9IO$: C, 46.48; H, 3.20. Found: C, 46.68; H, 3.24.

Ketone **27a**, colorless crystals, mp 71–72 °C: ν_{max}^{KBr} 1750 cm^{-1}; ^{1}H NMR (δ, CDCl 7.40 (dd, *J* = 8 and 1 Hz, 1 H), 7.15 (dd, *J* = 8 and 1 Hz, 1 H), 6.82 (d, *J* = 8 Hz, 1 H), 3.65 (m, 2 H), and 2.65–2.0 (br m, 4 H); ^{13}C NMR (ppm, $CDCl_3$) 211.07, 149.77, 144.55, 136.12, 129.14, 121.25, 91.27, 61.54, 49.64, 42.97, and 29.81; *m/e* calcd 283.9700, obsd 283.9707.

Anal. Calcd for $C_{11}H_9IO$: C, 46.48; H, 3.20. Found: C, 46.55; H, 3.10.

5-Cyanobenzonorbornen-2-one (27a). Reaction of **26a** (500 mg, 1.76 mmol) with sodium dicyanocuprate in dimethylformamide in the fashion described above furnished 300 mg (93%) of **27a,** colorless crystals, mp 99–100 °C (from methanol): ν_{max}^{KBr} 2210 and 1750 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 7.6–7.05 (m, 3 H), 4.01 (m, 1 H), 3.68 (m, 1 H), and 2.65–1.75 (br m, 4 H); ^{13}C NMR (ppm, $CDCl_3$) 210.70, 152.75, 141.46, 130.23, 127.62 (2C), 116.94, 106.50, 58.08, 50.67, 41.51, and 39.02; *m/e* calcd 183.0684, obsd 183.0688.

Anal. Calcd for $C_{12}H_9NO$: C, 78.66; H, 4.95. Found: C, 78.50; H, 5.01.

2,5-Dicyanobenzonorbornadiene (29a). The hydrazone of **27a** was obtained in 88% yield as a colorless solid, mp 87–88 °C. This unpurified product was converted to vinyl iodide **28a** in the usual manner. Chromatographic purification on silica gel afforded **28a** as a colorless solid, mp 73–75 °C: in 35% yield; ^{1}H NMR (δ, CDC l_3) 7.53–6.83 (m, 4 H), 4.16 (m, 1 H), 3.96 (m, 1 H), 2.65–2.53 (m, 1 H), and 2.31–2.16 (m, 1 H); *m/e* calcd 292.9703, obsd 292.9710.

A 370-mg (1.26 mmol) sample of **23a** was treated with cuprous cyanide in HMPA at 90–95 °C for 3 h to give a brown oil which was crystallized from methanol and sublimed to provide 200 mg (83%) of **29a** as colorless crystals, mp 124–125 °C: ν_{max}^{KBr} 2210 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 7.61–6.86 (m, 4 H), 4.43–4.33 (m, 1 H), 4.17 (m, 1 H), and 2.66–2.30 (m, 2 H); ^{13}C NMR (ppm, $CDCl_3$) 157.98 (2C), 152.78, 150.16, 128.46, 126.57 (2C), 116.68, 115.38, 107.58, 70.10. 53.60, and 51.12; *m/e* calcd 192.0687, obsd 192.0691.

Anal. Calcd for $C_{13}H_8N_2$: C, 81.22; H, 4.20. Found: C, 81.01; H, 4.41.

8-Cyanobenzonorbornenone (27b). Treatment of **26b** with sodium dicyano cuprate procedure **27b** in 78% yield as a colorless heavy oil: ^{1}H NMR (δ, $CDCl_3$) 7.53–6.15 (m, 3 H), 3.80 (m, 2 H), and 2.73–1.95 (m, 4 H); *m/e* calcd 183.0684, obsd 183.0690.

2,8-Dicyanobenzonorbornadiene (29b). The hydrazone of **27b** was obtained in quantitative yield. Conversion to vinyl iodide **28b** proceeded in 47% yield. Subsequent treatment with cuprous cyanide in HMPA (90–95 °C, 3 h) gave **29b** as colorless crystals, mp 116–117 °C, after recrystallization from methanol and sublimation: ν_{max}^{KBr} 2240 and 2220 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 7.56–6.86 (m, 4 H), 4.35 (m, 1 H), 4.19–4.12 (m, 1 H), and 2.65–2.30 (m, 2 H); ^{13}C NMR (ppm, $CDCl_3$) 159.39 (2C), 153.41, 149.39, 128.31, 126.76, 126.62. 116.70, 115.01, 107.58, 70.20, and 51.85; *m/e* calcd 192.0687. obsd 192.0691.

Anal. Calcd for $C_{13}H_8N_2$: C, 81.22; H, 4.20. Found: C, 80.82; H, 4.25.

General Photoisomerization Procedure. The mono- or disubstituted benzonorbornadiene was dissolved in benzene (50 mL) containing 2–3 drops of acetophenone and the solution was deoxygenated by bubbling nitrogen through the sample for 20 min. After being placed under a nitrogen atmosphere, the reaction mixture was irradiated at 3500 Å in a Rayonet apparatus for 20–40 min. The solvent and acetophenone were removed in vacuo and the residue was purified as indicated.

3-Cyanotetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (30). The crude photolysate from 100 mg of **10** was subjected to preparative thick-layer chromatography. Elution with pentane separated residual acetophenone from the single photoproduct **30** (92 mg, 92%). colorless crystals, mp 68–69 °C, after sublimation: ν_{max}^{KBr} 2190 cm^{-1}: ^{1}H NMR (δ, $CDCl_3$) 7.49–7.03 (m, 4 H), 3.69 (dd, *J* = 7.5 and 2.8 Hz, 1 H), 3.23 (d, *J* = 5.6 Hz, 1 H), 3.20–2.90 (ddd, *J* = 9.5, 7.5, and 4.2 Hz, 1 H), 2.83–2.70 (ddd, *J* = 5.6, 4.2, and 2.8 Hz, 1 H), and 0.82 (d, *J* = 9.5 Hz, 1 H); ^{13}C NMR (ppm, $CDCl_3$) 146.28, 137.64, 126.91, 126.47, 123.75, 120.35, 117.78, 46.27, 38.01, 37.67, 29.13, and 28.69; *m/e* calcd 167.0740, obsd 167.0739.

Anal. Calcd for $C_{12}H_9N$: C, 86.19; H, 5.43. Found: C, 85.91; H, 5.49.

3,10-Dicyanotetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (31a). The product from photoisomerization of **18** (100 mg) was recrystallized directly from methanol to give 90 mg (90%) of pure **31a,** colorless crystals, mp 159.5–160.5 °C: ν_{max}^{KBr} 2190 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 7.56 (pseudo s, 2 H), 7.34 (s, 1 H), 3.79 (dd, *J* = 7.5 and 2.8 Hz, 1 H), 3.34 (d, *J* = 5.7 Hz, 1 H), 3.23–3.08 (m, 1 H), 3.00–2.84 (m, 1 H), and 0.83 (d, *J* = 9.8 Hz, 1 H); ^{13}C NMR (ppm, $CDCl_3$) 147.25, 143.27, 131.81, 124.67, 123.70, 118.90, 116.66, 110.40, 45.93, 39.47, 37.72, 29.37, and 28.35; *m/e* calcd 192.0687, obsd 192.0691.

Anal. Calcd for $C_{13}H_8N_2$: C, 81.22; H, 4.20. Found: C, 80.96; H, 4.33.

3,9-Dicyanotetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (31b). Irradiation of 100 mg of **23** afforded a single photoisomer which was purified by recrystallization from methanol and identified as **31b**, colorless crystals, mp 170–171 °C (92 mg, 92%): ν_{max}^{KBr} 2190 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 7.71–7.13 (m, 3 H), 3.78 (dd, *J* = 7.6 and 2.8 Hz, 1 H), 3.32 (d, *J* = 5.6 Hz, 1 H), 3.24–3.04 (ddd, *J* = 9.7, 7.6, and 4.0 Hz, 1 H), 2.97–2.8 (ddd, *J* = 5.6. 4.0, and 2.8 Hz. 1 H), and 0.83 (d, *J* = 9.7 Hz, 1 H); ^{13}C NMR (ppm, $CDCl_3$) 151.28, 139.09, 131.28, 127.20, 121.23, 118.80, 116.66, 111.08, 46.32, 38.79, 37.14, 28.94, and 28.30; *m/e* calcd 192.0687, obsd 192.0691.

Anal. Calcd for $C_{13}H_8N_2$: C, 81.22; H, 4.20. Found: C, 80.85; H, 4.24.

3,11-Dicyanotetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (32b). The photolysate from photoisomerization of **29a** (100 mg) in the usual manner exhibited a single spot on thin-layer chromatography. Recrystallization from methanol gave pure **32** (85 mg, 85%) as colorless crystals, mp 156-157 °C; ν_{max}^{KBr} 2190 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 7.64-7.24 (m, 3 H), 3.79 (dd, J = 7.8 and 2.5 Hz, 1 H), 3.54 (d, J = 5.5 Hz, 1 H), 3.25-3.10 (m, 1 H), 3.03-2.90 (m, 1 H), and 0.85 (d, J = 9.5 Hz, 1 H); ^{13}C NMR (ppm, $CDCl_3$) 147.44, 142.25, 130.06, 127.39, 124.67, 117.25, 116.47, 108.65, 46.41, 39.62, 36.95, 29.47, and 28.35; *m/e* calcd 192.0687, obsd 192.0691.

Anal. Calcd for $C_{13}H_8N_2$: C, 81.22; H, 4.20. Found: C, 80.97; H, 4.20.

3,8-Dicyanotetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (32a). A 100-mg sample of **29b** was irradiated to give a single photoproduct which was purified by recrystallization from methanol. There was obtained 80 mg (80%) of **32a** as colorless crystals, mp 143-144 °C; ν_{max}^{KBr} 2190 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 7.72-7.23 (m, 3 H), 4.00 (dd, J = 7.8 and 2.6 Hz, 1 H), 3.34 (d, J = 5.6 Hz, 1 H), 3.25-3.06 (ddd, J = 9.8, 7.8, and 3.8 Hz, 1 H), 2.96-2.83 (ddd, J = 5.6, 3.8, and 2.6 Hz, 1 H), and 0.87 (d, J = 9.8 Hz, 1 H); ^{13}C NMR (ppm, $CDCl_3$) 149.97, 139.24, 129.53, 128.22, 127.98, 116.81, 116.57, 105.25, 45.44, 38.84, 37.58, 29.23, and 28.16; *m/e* calcd 192.0687, obsd 192.0691.

Anal. Calcd for $C_{13}H_8N_2$: C, 81.22; H, 4.20. Found: C, 81.10; H, 4.30.

Acknowledgment. This research was made possible by the financial support of the National Science Foundation (CHE 76-08764 to L.A.P. and CHE 76-11839 to K.N.H.) to whom we are grateful. We also thank Dr. Charles Cottrell for ^{13}C NMR measurements and C. R. Weisenberger for mass spectral data.

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