Polarized IR Spectroscopy of a Triplet 1,3-Biradical: The Structure of a Methylene-Bridged 1,8-Naphthoquinodimethane

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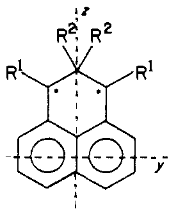
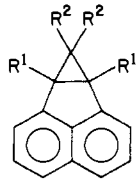
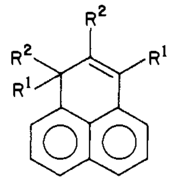
Few biradicals have been well characterized spectroscopically.[1] We report assignments of C_{2v} symmetry and C–H and C–D stretching frequencies for the triplet edge-to-edge trimethylene moiety in **1A–D**, on the basis of polarized IR spectra of matrix-isolated **1** oriented by photoselection.



1A-D

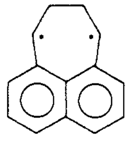


2A-D



3A-D

	A	B	C	D
R^1	H	H	D	D
R^2	H	D	D	H



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As a 1,8-naphthoquinodimethane, **1** belongs to a well-known class of non-Kekulé hydrocarbons.[2-5] **1A** has been prepared by UV irradiation of matrix-isolated **2A** and characterized by UV-visible absorption, fluorescence, and ESR.[2-4,6]

UV-visible and ESR spectra show that UV irradiation of the cyclopropanes **2A–D** in argon matrix yields the triplet biradicals **1A–D**, mixed with **3** and residual **2**. The IR spectra of **1A–D** have now been obtained from the difference before and after subsequent visible irradiation, which converts[2] **1** to **3**. They pinpoint the four C–H and C–D stretches of the trimethylene moiety (Figure 1). The thermal decay[2] of the IR, UV, and ESR signals in polyethylene matrix, observed at a series of selected temperatures (100–160 K), occurs at identical rates. Depending on the isotopic substitution and temperature, this leads to **2**, **3**,[7] or both:

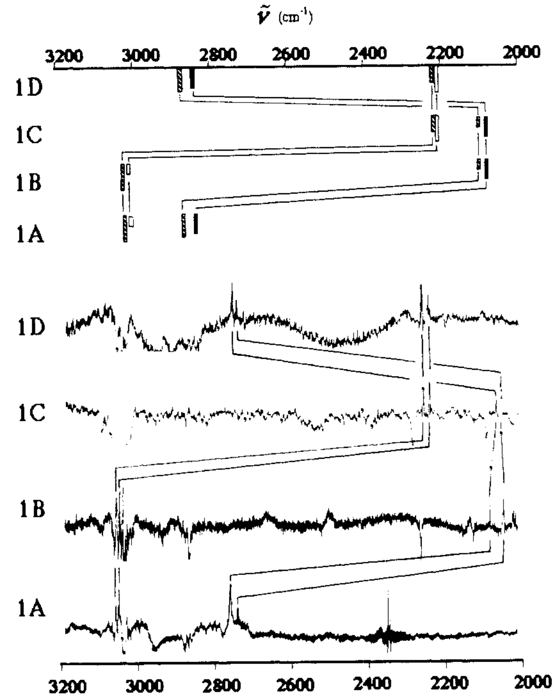
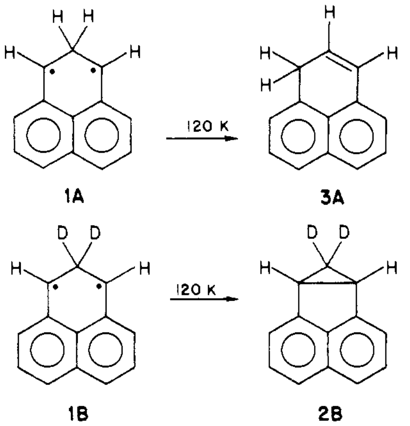


Figure 1. (Top) Calculated IR frequencies of **1A–1D** (MNDO, multiplicative correction factor 0.885) and polarizations: full bar, *x*; empty bar, *y*; dashed bar, *z*. (Bottom) Experimental IR spectra of **1A–1D** (positive peaks) and **3A–3D** (negative peaks). The straight lines identify the C–H and C–D stretching vibrations in the trimethylene moiety.



Two differently partially oriented samples of **1A** and **1C** were prepared by irradiation of random samples with linearly polarized laser light[8] at 496.5 nm, absorbed by a *y*-polarized transition in **1** [orientation factors[9] $K(y)$, Table I], and at 488.0 nm, absorbed by a *z*-polarized transition in **1** [$K(z)$]. The absolute polarizations of the two visible peaks agree with those[3] of the analogous peaks in **4**. They were determined from the dichroic absorption of **1** in stretched polyethylene[10,11] after it was produced by irradiation

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[1] We are aware of only one triplet biradical whose IR spectrum has been reported: Roth, W. R.; Biermann, M.; Erker, G.; Jelich, K.; Gerhartz, W.; Görner, H. *Chem. Ber.* **1980**, *113*, 586.

[2] Muller, J.-F.; Muller, D.; Dewey, H. J.; Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 1629.

[3] Gisin, M.; Rommel, E.; Wirz, J.; Burnett, M. N.; Pagni, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 2216.

[4] Cofino, W. P.; van Dam, S. M.; Kamminga, D. A.; Hoornweg, G. Ph.; Gooijer, C.; MacLean, C.; Velthorst, N. H. *Spectrochim. Acta, Sect. A* **1984**, *40A*, 219.

[5] Pagni, R. M.; Watson, C. R., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2291. Watson, C. R., Jr.; Pagni, R. M.; Dodd, J. R.; Bloor, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 2551. Gisin, M.; Wirz, J. *Helv. Chim. Acta* **1976**, *59*, 2273. Pagni, R. M.; Burnett, M. N.; Dodd, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 1972. Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297. Chisholm, W. P.; Weissman, S. I.; Burnett, M. N.; Pagni, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 7103. Döhnert, D.; Koutecký, J. *J. Am. Chem. Soc.***1980**, *102*, 1789. Pagni, R. M.; Burnett, M. N.; Hassaneen, H. M. *Tetrahedron* **1982**, *38*, 843. Platz, M. S.; Carrol, G.; Pierrat, F.; Zayas, J.; Auster, S. *Tetrahedron* **1982**, *38*, 777. Cofino, W. P.; van Dam, S. M.; Hoornweg, G. Ph.; Gooijer, C.; MacLean, C.; Velthorst, N. H.; Pagni, R. M. *Spectrochim. Acta, Sect. A* **1984**, *40A*, 251. Hasler, E.; Gassmann, E.; Wirz, J. *Helv. Chim. Acta* **1985**, *68*, 777. Fritz, M. J.; Ramos, E. L.; Platz, M. S. *J. Org. Chem.* **1985**, *50*, 3522.

[6] The original assignment of the ground state as singlet[2] was based on ESR at temperatures where **1** is not entirely stable. Lower temperature work[3] has since established the triplet as the ground state, and we have now verified this for **1A–D**.

[7] A kinetic study of the thermal isomerization of **1A** to **3A** over a limited temperature range has been reported previously.[2]

[8] E.g.: Albrecht, A. C. *Mol. Spectrosc.* **1961**, *6*, 84 and ref 10. For previous use of the technique for argon-matrix-isolated species, see, e.g.: Burdett, J. K.; Grzybowski, J. M.; Perutz, R. N.;Poliakoff, M.; Turner, J. J.; Turner, R. F. *Inorg. Chem.* **1978**, *17*, 147.

[9] For the *i*th transition moment, $K_i = \langle \cos^2 i \rangle$. The angular brackets indicate averaging and *i* is the angle between the *i*th transition moment and the direction *Z* of the electric vector of the laser light ($K_x + K_y + K_z = 1$). $K_i = d_i/(2 + d_i)$, where $d_i = E_Z/E_Y$ is the dichroic ratio.

[10] Michl, J.; Thulstrup, E. W. *Spectroscopy with Polarized Light*; VCH Publishers, Inc.: Deerfield Beach, FL, 1986.

[11] For technique see: Thulstrup, E. W.; Michl, J. *J. Am. Chem. Soc.* **1982**, *104*, 5594. Radziszewski, J. G.; Michl, J. *J. Am. Chem. Soc.*, in press.

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Table I. IR Vibrations of Triplet 1,3-Perinaphthadiyl and Their Polarizations

	exptl				calcd[a]	
compd	$\tilde{\nu}$, cm^{-1}	$K(y)$	$K(z)$	sym	$\tilde{\nu}$, cm^{-1}	sym
1A	2742	0.36	0.44	x	2824	x
	2761	0.33[b]	0.22	z	2885	z
	3056	0.28	0.39	y	3011	y
	3066	0.35	0.19	z	3016	z
	$K_y(y) = 0.26$ $K_x(y) = K_z(y) = 0.37$[c]					
	$K_z(z) = 0.23$ $K_x(z) = K_y(z) = 0.39$[c]					
1C	2046	0.38	0.41	x	2081	x
	2061	0.35	0.26	z	2088	z
	2237	0.22	0.36	y	2208	y
	2253	0.39	0.23	z	2212	z
	$K_y(y) = 0.24$ $K_x(y) = K_z(y) = 0.41$[c]					
	$K_z(z) = 0.22$ $K_x(z) = K_y(z) = 0.38$[c]					

[a] MNDO, corrected by a multiplicative factor of 0.885, obtained by fitting the CH_2 *as* stretch in propane. [b] Subject to a large experimental uncertainty. [c] From the dichroic ratios of about 20 IR bands. Some of the small difference between $K_x(y)$ and $K_z(y)$ and between $K_x(z)$ and $K_y(z)$ is probably due to slightly mixed polarization of the absorption at 496.5 and 488 nm. This has no effect on the proposed assignments and C_{2v} symmetry.

of **2** at 10 K. The orientation of **2** was known from its UV dichroism.

Dichroic ratios of the approximately 20 IR bands of oriented **1A** and **1C** yielded the six orientation factors for each, $K_u(y)$ and $K_u(z)$, $u = x,y,z$. These are only compatible with C_{2v} symmetry and give an unequivocal assignment of the four stretching vibrations (Table I).[12]

It has been proposed[4] that the CH_2 group in **1A** is tilted out of the aromatic plane (C_s symmetry), although the two β protons are equivalent in the (poorly resolved) ESR spectrum. Such a geometry has been claimed to result from MNDO and molecular mechanics calculations.[4] Our polarization results clearly establish C_{2v} as the symmetry of both **1A** and **1C**, and this agrees with the absence of peak doubling and with our UHF MNDO geometry optimization.

The observed α C–H stretches are virtually identical with that of the isopropyl radical,[13] which is split and occurs at 3058 and 3069 cm^{-1}. The β C–H stretches are at strikingly low frequencies. In particular, the CH_2 *as* stretch, ordinarily[14] at 2853 ± 10 cm^{-1}, occurs at 2742 cm^{-1} in **1A**. The 111-cm^{-1} hyperconjugation shift is thus considerably larger than expected from a comparison with the 40-cm^{-1} shift in the *n*-propyl[13] radical (2812.5 cm^{-1}), which has a full unpaired unit spin adjacent to the CH_2 group. In **1** only about half of a unit spin resides on each radical center, judging both by calculations and by the ESR coupling constants.[2] If the orientation of the CH_2 group relative to the $2p\pi$ orbital on CH were the same in both compounds, one might expect a comparable shift. Perhaps the conformations differ, or it is far more effective to have half a spin on each side of the CH_2 group than a full spin on one side, because of the allylic resonance in the no-bond structure (phenalenyl is particularly stabilized).

MNDO calculations (Figure 1, Table I) reproduce the order of the *s* and *as* combinations of both the α and the β C–H stretches in **1** but underestimate the difference between the α and the β stretches and do not reproduce the large shift of the CH_2 *as* stretch in **1** although they presumably take full account of the special stability of phenalenyl. A crude comparison also can be made with published ab initio calculations[15] on the parent edge-to-edge $\cdot CH_2CH_2CH_2\cdot$ triplet. The calculated *s* and *as* stretches of the central CH_2 group are now in the opposite order than found in **1**. With a multiplicative correction factor of 0.892, fitted to the *as* CH_2 stretch of cyclopropane, the CH_2 *as* stretch is predicted at 2824 cm^{-1}, so that the striking shift we observe in **1** is again not reproduced. Thus, the observed very low frequency of the β C–H stretch in **1** does not currently have a satisfactory quantitative interpretation.

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(12) For molecules of **1** remaining after photoselection on an absorbing visible $\pi\pi^*$ transition moment oriented in the naphthalene plane along z, we have $K_z(z) < K_y(z) = K_x(z)$. For either C_{2v} or C_s symmetry $K_y(z)$ is determined unequivocally as 0.39 in **1A** and 0.36 in **1C**, requiring $K_x(z) = 0.39$, $K_z(z) = 0.22$ and $K_x(z) = 0.36$, $K_z(z) = 0.28$, respectively. The dichroism of the *s* and *as* CH_2 or CD_2 vibrations reflects the orientation of the methylene group relative to z and to the out-of-plane axis x; for a transition polarized in the xz plane at angle ϕ to z, $\tan^2 \phi = (K_z - K_x)/(K_y - K_x)$. Within the experimental error of 0.02–0.03, the data in Table I are only compatible with a z polarization of the CH_2 and CD_2 *s* stretches ($\phi = 0^0$) and x polarization of the *as* stretches ($\phi = 90°$).

(13) Pacansky, J.; Brown, D. W.; Chang, J. S. *J. Phys. Chem.* **1981**, *85*, 2562.

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(15) Yamaguchi, Y.; Osamura, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1983**, *105*, 7506.

Preparatively Useful Dehydrogenative Method for Dodecahedrane Synthesis

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Considerable attention remains focused on dodecahedrane (**2**) and its functional derivatives because these spherical molecules represent potentially useful tools for probing varied chemical phenomena in a unique way. In 1982, a successful synthesis of the parent hydrocarbon was achieved by the Paquette group.[1] The pivotal final step consisted of heating an intimate mixture of secododecahedrane (**1**) with hydrogen-presaturated 10% palladium on carbon at 250 °C for several hours.[2] The undesirable features of this otherwise remarkable ring closure are its modest efficiency (40–50% yield), severe limitation on throughout (maximum of 2 mg of **1** per run), and intolerance of pendant groups.[3] We have now developed a superior, preparatively useful dehydrocyclization system. The exceptional promise offered by this new process projects us from the era of concern over dodecahedrane construction[4] to the next evolutionary stage involved with assessing the chemical reactivity of this class.

The earlier complications stem in large part from the presence of excess hydrogen, which proved necessary to curtail the propensity of Pd(0) for 1,2-dehydrogenative elimination. Optimal alternative conditions were regarded to be those wherein one transition metal would effect smooth transannular C–C bond formation in the presence of a second metal capable of absorbing the liberated H_2 at elevated temperatures. Zerovalent titanium

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(1) (a) Ternansky, R. J.; Balogh, D. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 4503. (b) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Kentgen, G. *Ibid.* **1983**, *105*, 5446.

(2) For analogous C–C forming reactions, consult: (a) Rylander, P. N. *Organic Synthesis with Noble Metal Catalysts*; Academic Press: New York, 1973; p 28. (b) Kazanskii, B. A.; Balenkova, E. S.; Khromov, S. I. *Russ. Chem. Rev.* (*Engl. Transl.*) **1967**, *36*, 866. (c) Burns, W.; McKervey, M. A.; Mitchell, T. R. B.; Rooney, J. J. *J. Am. Chem. Soc.* **1978**, *100*, 906. (d) Crawford, M.; Supanekar, V. R. *J. Chem. Soc.* **1964**, 2380. (e) Pozdmikina, S. G.; et al. *Chem. Abstr.* **1973**, *79*, 31564x.

(3) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Taylor, W. J. *J. Am. Chem. Soc.* **1983**, *105*, 5441.

(4) (a) Eaton, P. E. *Tetrahedron* **1979**, *35*, 2189. (b) Baldwin, J. E.; Beckwith, P. L. M. *J. Chem. Soc., Chem. Commun.* **1983**, 279. (c) Eaton, P. E.; Bunnelle, W. H.; Engel, P. *Can. J. Chem.* **1984**, *62*, 2612.

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