and molecular quadrupole moments of 1,3-cyclohexadiene. These results are then compared with other small rings and planar molecules.

The microwave spectrum of 1,3-cyclohexadiene has been assigned previously,[22] and we observed the $1_{11} \rightarrow 2_{12}$, $1_{10} \rightarrow 2_{11}$, and $1_{01} \rightarrow 2_{02}$ $\Delta M = 0$ and $\Delta M = \pm 1$ rotational transitions (in the gas phase) at magnetic fields near 21,000 G. The high-field electromagnet which gives fields of up to 30,000 G over a 6-ft length and the phase-stabilized microwave spectrograph and frequency sweep system used in this work have also been described previously.[16] The spectra were recorded at about 230°K and the results are listed in Table I. A least-squares fit of the experimental data given in Table I gives the five independent Zeeman parameters (the molecular g values, g_{aa}, g_{bb}, g_{cc}, and the magnetic susceptibility anisotropies, $(2\chi_{aa} - \chi_{bb} - \chi_{cc})$ and $(2\chi_{bb} - \chi_{aa} - \chi_{cc})$) listed in Table II.[23] The molecular electric quadrupole moments, Q_{xx}, are directly related to the molecular g values and magnetic susceptibility anisotropies.[15] The resultant values of the quadrupole moments are listed in Table II. We note that the molecular quadrupole moments in 1,3-cyclohexadiene are nearly identical with the values in benzene.[20] The methods of determining the remaining numbers in Table II have all been explained previously.[14-21] Thus, using the approximate molecular structure[22] and the known bulk susceptibility[24] leads to the remaining numbers in Table II.

Table I. High-Field Frequency Shifts from ν^a of Several Rotational Transitions in 1,3-Cyclohexadienes

Transition	$M_J \rightarrow$	M_J'	$\Delta\nu$(obsd), kHz	$\Delta\nu$(calcd), kHz	$\Delta\Delta\nu$, kHz	H, G
$1_{11} \rightarrow 2_{12}$	1	2	−180	−162	−18	21,034
(13,167.43)	−1	−2	+262	252	10	
	−1	−1	−176	−154	−22	20,960
	0	0	−16	−11	−5	
	1	1	−16	9	−25	
$1_{01} \rightarrow 2_{02}$	1	2	−100	−124	24	21,015
(17,179.03)	−1	−2	+240	238	2	
	−1	−1	−164	−167	3	20,977
	0	0	4	−36	−40	
	1	1	4	48	−44	
$1_{10} \rightarrow 2_{11}$	0	1	−684	−672	−12	21,041
(17,888.67)	1	2	−500	−498	−2	
	−1	−2	496	511	−15	
	0	−1	496	501	−5	
	0	0	−19	−61	42	20,971

[a] The zero-field frequencies (ν_0) are given (in parentheses) in MHz directly under the transition designation. The calculated results are with the Zeeman parameters listed in Table II.

Table II. Molecular Zeeman Parameters, Molecular Quadrupole Moments, Magnetic Susceptibilities, and the Second Moment of the Electronic Charge Distribution in 1,3-Cyclohexadiene[a]

$g_{aa} = -0.0400 \pm 0.0024$
$g_{bb} = -0.0433 \pm 0.0011$
$g_{cc} = -0.0062 \pm 0.0009$
$2\chi_{aa} - \chi_{bb} - \chi_{cc} = 5.73 \pm 1.6$
$2\chi_{bb} - \chi_{aa} - \chi_{cc} = 9.09 \pm 2.2$
$Q_{aa} = 2.68 \pm 2.8$
$Q_{bb} = 3.20 \pm 2.8$
$Q_{cc} = -5.88 \pm 3.8$
$\chi_{aa}^p = 284.97 \pm 1.3$
$\chi_{bb}^p = 284.55 \pm 1.0$
$\chi_{cc}^p = 512.01 \pm 1.0$

$\chi = {}^1/_3(\chi_{aa} + \chi_{bb} + \chi_{cc}) = -48.6$
$\chi_{aa} = -46.69 \pm 0.8$
$\chi_{bb} = -45.57 \pm 1.0$
$\chi_{cc} = -53.54 \pm 1.2$
$\chi_{aa}^d = -331.66 \pm 1.7$
$\chi_{bb}^d = -330.12 \pm 1.3$
$\chi_{cc}^d = -565.55 \pm 2.0$
$\langle a^2 \rangle = 66.45 \pm 0.7$
$\langle b^2 \rangle = 66.80 \pm 0.7$
$\langle c^2 \rangle = 11.34 \pm 0.7$

[a] The a axis contains the electric dipole moment and the c axis is out of the molecular plane. χ is in units of 10^{-6} erg/G^2 mole, Q is in units of 10^{-26} esu cm^2, and $\langle a^2 \rangle$ is in units of 10^{-16} cm^2.

Table III. Values of the Magnetic Susceptibility Anisotropy (in units of 10^{-6} erg/G^2 mole) for a Wide Range of Small Molecules[a]

Molecule	$\chi_{zz} - {}^1/_2(\chi_{xx} + \chi_{yy})$	Ref
Benzene	−59.7	3
Fluorobenzene	−58.3 ± 0.8	17
Thiophene	−50.1 ± 1.0	20
Pyrrole	−42.4 ± 0.5	*b*
Furan	−38.7 ± 0.5	20
Cyclopropene	−17.0 ± 0.5	*c*
Ethylene sulfide	−15.4 ± 0.4	19
Ethylenimine	−10.9 ± 0.7	*b*
Ethylene oxide	−9.4 ± 0.4	18
1,3-Cyclohexadiene	−7.4 ± 2.2	This work

[a] The z axis is perpendicular to the molecular plane. [b] D. H. Sutter and W. H. Flygare, unpublished results. [c] R. C. Benson and W. H. Flygare, *J. Chem. Phys.*, in press.

The surprising result of this work is the extremely small magnetic susceptibility anisotropy in the 1,3-cyclohexadiene molecule. This large difference is put into proper perspective in Table III where the experimental values of $\chi_{zz} - {}^1/_2(\chi_{xx} + \chi_{yy})$ are listed for a series of ring compounds which have been recently determined.

The dramatic difference between the values of $\chi_{zz} - {}^1/_2(\chi_{xx} + \chi_{yy})$ for 1,3-cyclohexadiene and benzene (as well as the other aromatic ring compounds) leaves little doubt that a substantial ring current exists in aromatic compounds. Indeed, the magnetic susceptibility anisotropies listed in Table III may be useful in establishing a criterion for aromatic character.[25,26]

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(22) S. S. Butcher, *J. Chem. Phys.*, 42, 1830 (1965).

(23) The necessary equations and methods used to extract the five Zeeman parameters are shown in ref 14–21.

(24) G. W. Smith, "A Compilation of Diamagnetic Susceptibilities," General Motors Corporation Research Report, GMR-317, 1960.

(25) See A. J. Jones, *Rev. Pure Appl. Chem.*, **18**, 253 (1968), for a current review.

(26) H. J. Dauben, Jr., J. D. Wilson, and J. L. Laity, *J. Am. Chem. Soc.*, **91**, 1991 (1969).

(27) Petroleum Research Fund Predoctoral Fellow.

Isomerization of *o*-Biphenylyl Isocyanide into 1-Azabenz[*b*]azulene and the Formation of Both from *o*-Biphenylyl Isothiocyanate[1]

Sir:

The formation of 1-azabenz[*b*]azulene[2] (**2**) by the irradiation of *o*-biphenylyl isocyanide (**1**) is a new reaction which reveals electrophilic carbenoid properties of the aromatic isocyanide group.[3] This appears to be

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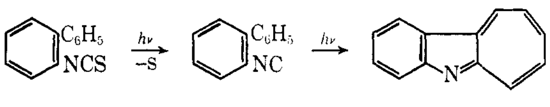
(1) Financial assistance from NASA Grant No. NGR 14-012-004 is acknowledged.

(2) (a) C. W. Muth, D. O. Sterninger, and Z. B. Papanastassiou, *J. Am. Chem. Soc.*, 77, 1006 (1955); (b) A. G. Anderson, Jr., and J. Tazuma, *ibid.*, 74, 3455 (1952).

(3) W. Kirmse ("Carbene Chemistry," Academic Press, New York,

the first example of an aromatic ring expansion brought about by an insertion of an isocyanide carbon atom.



3 1 2

The isocyanide **1**, obtained from the corresponding formamidobiphenyl by dehydration,[4] is a colorless liquid,[5] bp 113–114° (1.5 mm), $n^{22}\mathrm{D}$ 1.6115, ir (neat) 2130 cm^{-1} (NC). *Anal.* Calcd for $C_{13}H_9N$: C, 87.15; H, 5.03; N, 7.82; mol wt, 179. Found: C, 87.17, H, 5.32; N, 7.88; M$^+$ 179. After irradiation at 2537 Å for 19 hr, **1** in cyclohexane is transformed into 1-azabenz[*b*]azulene (**2**) in 62% yield based on recovered **1**. The product **2** is obtained as a dark red-purple solid, mp 134.5–136° (sealed tube), methiodide mp 232°.[2,6,7]

Formation of the azulene **2** from the isocyanide **1** was first revealed when both **1** and **2** were found to be produced from *o*-biphenylyl isothiocyanate (**3**).[8] After irradiation of **3** in cyclohexane at 2537 Å for 64 hr, *o*-biphenylyl isocyanide (**1**), 1-azabenz[*b*]azulene (**2**), and sulfur were obtained in corresponding yields of 25, 28, and 24% based on recovered **3**.

It appears that irradiation may develop electrophilic carbenoid properties in an isocyanide function. In addition to theoretical interest in this carbenoid species, there is potential value in synthetic work insofar as the isocyanide may be prepared *in situ* from the corresponding isothiocyanate, thereby minimizing exposure to an isocyanide, which may be malodorous and/or toxic. Other electrophilic carbenoid reactions of isocyanides are under investigation.

N. Y., 1964, p 203) attributes to resonance a certain stability for isocyanides "which display no electrophilic reactivity and behave more or less actively as nucleophiles."

(4) By adapting a general procedure reported by I. Ugi and R. Meyer, *Chem. Ber.*, **93**, 239 (1960), dehydration with phosphorus oxychloride gave the isocyanide 1 in 65% yield.

(5) I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer, and K. Offermann [*Angew. Chem.*, 77, 492 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 472 (1965)] reported 1 as a solid, mp 116–118°, apparently in error.

(6) W. Treibs, R. Steinert, and W. Kirchof, *Ann.*, **581**, 54 (1953).

(7) Elemental analyses and molecular weight determinations were in agreement with structure 2. Uv and ir absorption data were in complete agreement with previously reported data.[2,6]

(8) According to a general procedure described by J. C. Jochims, *Chem. Ber.*, **101**, 1746 (1968), the isothiocyanate 3 was prepared from *o*-biphenylylamine, dicyclohexylcarbodiimide, and carbon disulfide in 75% yield as a colorless liquid, bp 130–132 (0.25 mm), $n^{26}\mathrm{D}$ 1.6805. *Anal.* Calcd for $C_{13}H_9NS$: C, 73.90; H, 4.29; N, 6.63; S, 15.13; mol wt, 211. Found: C, 74.25; H, 4.49; N, 6.75; S, 15.00; M$^+$ 211.

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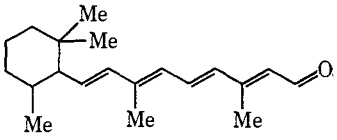
A New Series of Synthetic Visual Pigments from Cattle Opsin and Homologs of Retinal

Sir:

We have already reported the synthesis of 5,6-dihydroretinal (I)[1] and the successful coupling of an irradiated sample of I with cattle opsin to yield a synthetic visual pigment, $\lambda_{\max}$ 465 mμ.[2] Since then we have characterized this to be a mixture of pigments derived from 9-*cis*-I and 11-*cis*-I. The details are being published elsewhere.[3] In continuation of our efforts to map the activity of the visual pigment chromophores, we have synthesized a number of polyene aldehydes and examined their reactivity toward cattle opsin.

Compounds I–VII were synthesized using suitable procedures. I was obtained as described earlier:[1] low-melting solid; uv $\lambda_{\max}^{\mathrm{EtOH}}$ 363 mμ; ir (neat) 2720, 1648, 1585, 965 cm^{-1}; mass spectrum, molecular ion at *m/e* 286 ($C_{20}H_{30}O$, 286). II (mp 104–106°; uv $\lambda_{\max}^{\mathrm{EtOH}}$ 349 mμ (lit.[4] mp 107–108°) was obtained by Wittig reaction of *all-trans*-2,4,6-octatrienal with triethyl phosphonoacetate followed by reduction ($LiAlH_4$) and oxidation (MnO_2).[5] III was synthesized by self-condensation of crotonaldehyde, mp 164–166° (lit.[6] mp 159–161°); $\lambda_{\max}^{\mathrm{MeOH}}$ 382 mμ. IV was prepared[7] from β-ionone: bp 104–105° (0.08 mm). V was prepared as described earlier. The reaction of V with triethyl phosphonoacetate followed by reduction ($LiAlH_4$) afforded 7-(2,2,6-trimethylcyclohexyl)-5-methyl-2,4,6-heptatrien-1-ol as a pale yellow oil: uv



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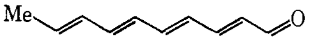

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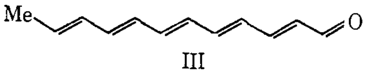

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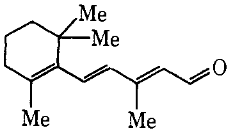

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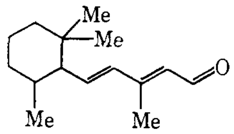

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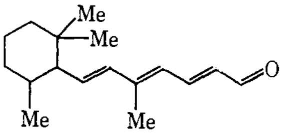

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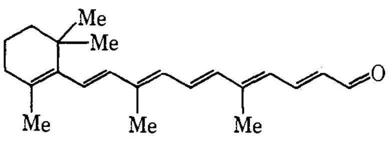

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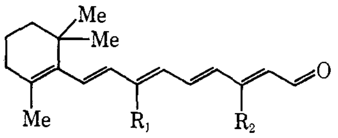

VIIIa, $R_1 = H; R_2 = CH_3$
b, $R_1 = CH_3; R_2 = H$
c, $R_1 = R_2 = H$

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