Table II

Eluent	Fraction no.	Prodt compn
Benzene	1–3	Nil
Benzene	4	Solid (mp 110–143°)
Benzene	5	Solid (mp 116–156°)
Benzene	6	Solid (mp 118–163°)
Benzene	7	Solid (mp 119–174°)
Benzene	8	Solid (mp 162–180°)
Benzene	9–13	Nil
Chloroform in benzene		
10%	14–18	Nil
20%	19–23	Nil
30%	24–27	Nil
40%	27–29	Solid (mp 219–220°)
50%	29–31	Nil

bonyl absorption at 5.73 μ (CHCl$_3$). The nmr spectrum showed aromatic protons (δ 7.20, 15 H) and methine protons (δ_A 4.96, δ_B 5.44, J_{AB} = 7.0 cps). The mass spectrum showed peaks at m/e 299 (M$^+$, 30.0), 182 (18.6), 181 (100), 180 (86.0), 179 (24.4), 178 (14.0), and 165 (8.4).

Anal. Calcd for C$_{21}$H$_{17}$NO: C, 84.29; H, 5.69; N, 4.68. Found: C, 84.35; H, 5.71; N, 4.74.

The filtrate was concentrated under reduced pressure giving a solid (0.9 g). The fourth recrystallization from isopropyl alcohol gave *trans*-1,3,4-triphenyl-2-azetidinone (700 mg, 2.3%, mp 127–128°). The infrared spectrum showed carbonyl absorption at 5.73 μ, and the nmr spectrum showed aromatic protons (δ 7.30, 15 H) and two methine protons as an AB pattern (δ_A 4.25, δ_B 4.94, J_{AB} = 3.0 cps). The mass spectrum showed peaks at m/e 299 (M$^+$, 9.8), 181 (33.8), 180 (100), 179 (22.8), 178 (13.1), and 165 (7.8).

Anal. Calcd for C$_{21}$H$_{17}$NO: C, 84.29; H, 5.69; N, 4.68. Found: C, 84.42; H, 5.70; N, 4.66.

Recrystallization of fractions 27–29 from benzene–pentane gave colorless crystals tentatively identified as 3,4-diphenyl-3,4-dihydrocarbostyril (0.15 g, 5.0%, mp 219–220°); infrared spectrum (KBr) 2.87 (broad), 5.98, 6.28, 6.72, 6.89, 7.32, 13.10, 13.65, and 14.28; nmr (CDCl$_3$), one-proton singlet at 9.35, an aromatic multiplet centered at 7.10, and an AB proton pattern, δ_A 4.17, δ_B 4.43 (J_{AB} = 6.0 cps). The mass spectrum exhibited an intense molecular ion at m/e 299 (100%) and fragment ions at m/e 78 (40.0%) and 180 (67.0%).

Anal. Calcd for C$_{21}$H$_{17}$NO: C, 84.29; H, 5.69; N, 4.68. Found: C, 84.25; H, 5.79; N, 4.75.

trans-1,3,4-Triphenyl-2-azetidinone. To a solution of benzalaniline (1.81 g, 0.01 mol) and triethylamine (1.0 g, 0.01 mol) in anhydrous ether (35 ml) was added dropwise a solution of α-phenylacetyl chloride (1.55 g, 0.01 mol) in ether (15 ml). A precipitate formed immediately, and the mixture was stirred for 0.5 hr. The reaction mixture was filtered and the filtrate was evaporated giving an oily residue. The oil was dissolved in a small volume of dichloromethane and poured onto 1.0 × 20 in. column prepared with 50 g of silica gel. The column was eluted with benzene (250 ml) which upon evaporation afforded an oil. Crystallization from isopropyl alcohol gave *trans*-1,3,4-triphenyl-2-azetidinone, 180 mg, 6%, mp 127–128° (lit.[11] mp 133–134°). The infrared spectrum (KBr) of the product was superimposable on that of the *trans*-β-lactam isolated from the irradiation of *cis*-α-phenylcinnamanilide. A mixture melting point determination showed no depression.

Nuclear Magnetic Resonance Studies of 1,3-Butadienes.[1] III. Bromoprene, Iodoprene, 1,1,3-Trichlorobutadiene-1,3, and 1,1,3-Tribromobutadiene-1,3

A. A. Bothner-By and D. Jung

*Contribution from the Mellon Institute, Pittsburgh, Pennsylvania 15213.
Received October 25, 1967*

Abstract: The proton nuclear magnetic resonance spectra of the title compounds at several temperatures have been recorded and analyzed completely. From these data, as well as ultraviolet spectral data, it is deduced that the haloprenes are largely in the *s-trans* conformation, while the trihalobutadienes are largely in a skew conformation.

The form of the potential energy curve for internal rotation about the central single bond in butadienes is as yet unknown, although evidence has been put forward that the *s-trans* form (Figure 1) is predominant in butadiene itself (microwave,[2] calorimetric,[3] infrared and Raman,[4] electron diffraction[5] studies) as well as in isoprene (microwave,[2] ir and Raman[4]), 2,3-dimethylbutadiene (microwave[2]), chloroprene (ir[6]), 2,3-dichloro-

butadiene (ir[6]), 1,1,4,4-tetrafluorobutadiene (microwave,[7] nmr[8]), and a number of substituted butadienes with hydrogens in positions 2 and 3 (nmr[1]). On the other hand, evidence has been reported indicating that a non-*s*-transoid conformation predominates in hexachlorobutadiene (uv,[9] Raman,[10] ir[6]), hexafluorobutadiene (ir and Raman[11]), 2-*t*-butylbutadiene (chemical kinetics,[12] nmr[13]), 2,3-di-*t*-butylbutadiene (chemical

(1) Paper II of this series: A. A. Bothner-By and R. K. Harris, *J. Am. Chem. Soc.*, 87, 3451 (1965).

(2) D. R. Lide, Jr., *J. Chem. Phys.*, 37, 2074 (1962); D. R. Lide, Jr., and M. Jen. *ibid.*, 40, 252 (1964).

(3) J. G. Aston, G. Szasz, H. W. Woolley, and F. G. Brickwedde, *ibid.*, 14, 67 (1946).

(4) D. J. Marais, N. Sheppard, and B. P. Stoicheff, *Tetrahedron*, 17, 163 (1962); K. Bradacs and L. Kahovec, *Z. Physik Chem.*, 48B, 63 (1940); N. V. Tarasova and L. M. Sverdlov, *Opt. Spectry.*, 21, 176 (1966).

(5) V. Schomaker and L. Pauling, *J. Am. Chem. Soc.*, 61, 1769 (1939); A. Almenningen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, 12, 1221 (1958).

(6) G. Szasz and N. Sheppard, *Trans. Faraday Soc.*, 49, 358 (1953).

(7) R. A. Beaudet, *J. Am. Chem. Soc.*, 87, 1390 (1965).

(8) K. L. Servis and J. D. Roberts, *ibid.*, 87, 1339 (1965).

(9) A. Roedig and R. Kloss, *Ann.*, 612, 1 (1958); M. I. Batuev and A. D. Matveeva, *Zh. Obshch. Khim.*, 28, 2903 (1958); *Izv. Akad. Nauk, SSSR*, 1393 (1958).

(10) K. W. F. Kohlrausch and H. Wittek, *Ber.*, 75, 227 (1942).

(11) J. C. Albright and J. R. Nielsen, *J. Chem. Phys.*, 26, 370 (1957).

(12) D. Craig, J. J. Shipman, and R. B. Fowler, *J. Am. Chem. Soc.*, 83, 2885 (1961).

(13) R. T. Hobgood and J. H. Goldstein, *J. Mol. Spectry.*, 12, 76 (1964).
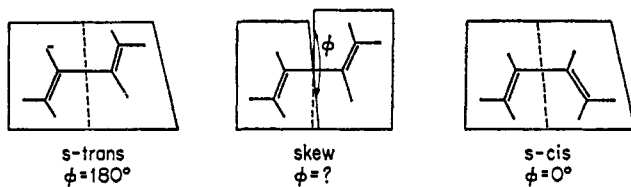
Figure 1. Designation of rotational conformers in butadienes.
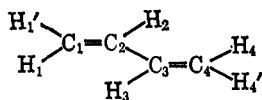

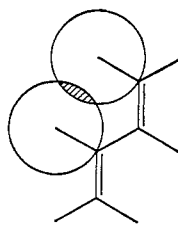Figure 2. Numbering scheme used for hydrogens and substituents.

Figure 3. Steric interference of substituents in the 1,3 positions of s-trans-butadienes.

kinetics,[14] uv,[15] nmr[15]), 2,4-dimethyl-1,3-pentadiene, and 2-chloro-4-methyl-1,3-pentadiene (uv[16]). While in many cases[3,5,8,16,17] it has been either explicitly or implicitly assumed that the stable nontransoid form of open-chain butadienes is the planar s-cis form, the evidence in those cases where a non-s-transoid form predominates generally points to[9,13,15,16] or is at least consistent with[10-12,14] a skew form. The present research was undertaken with the idea of obtaining substituted butadienes which might exist as a mixture of rotamers, and to study their behavior as a function of temperature, solvent, etc., in order to learn something about the shape of the potential energy curve.

In order to describe the placement of substituents and their spatial relationships the numbering scheme given in Figure 2 will be retained,[1] as will the designations ^2J, ^3J_c, ^3J_t, ^3J_s, ^4J_c, ^4J_t, $^5J_{cc}$, $^5J_{ct}$, $^5J_{tt}$ previously employed.[1]

Braude[16] has pointed out that interaction between bulky substituents in the 1,3 (or 2,4) positions can destabilize the s-trans form (Figure 3), and this factor is present in each of the non-s-trans cases cited above. Considering that chloroprene is predominantly s-trans while 2-t-butylbutadiene is predominantly non-s-trans, it appeared attractive to investigate bromoprene and iodoprene as possible intermediate cases. 1,1,3-Trichlorobutadiene-1,3 and 1,1,3-tribromobutadiene-1,3 have also been prepared and studied in the hope that they might represent cases where the rotamers are of nearly equal energy. The evidence presented here, however, indicates that in each of these four compounds a single rotamer predominates: in the cases of bromo-
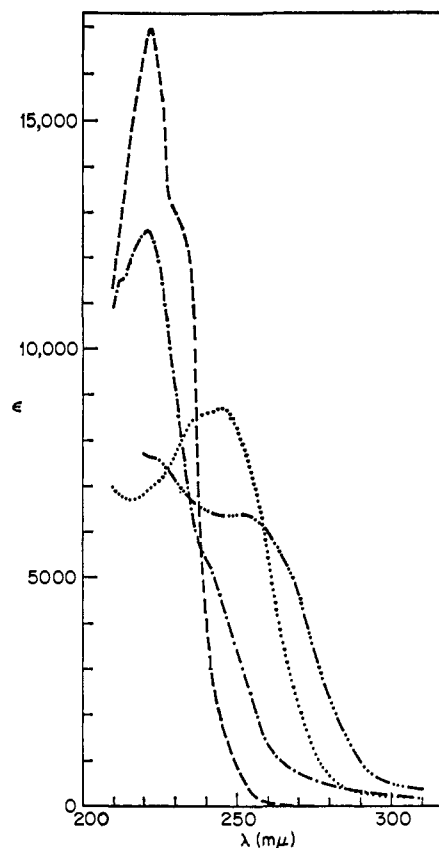
(14) H. J. Backer, Rec. Trav. Chim., 58, 643 (1939).
(15) H. Wynberg, A. de Groot, and P. W. Davies, Tetrahedron Letters, 1083 (1963).
(16) E. A. Braude, Experientia, 11, 457 (1955).
(17) R. S. Mulliken. J. Chem. Phys., 7, 121 (1939).

Figure 4. Uv absorption spectra of halogenated butadienes in cyclohexane solution: - - -, 2-bromobutadiene; —·—·—, 2-iodobutadiene; ····, 1,1,3-trichlorobutadiene; —···—···, 1,1,3-tribromobutadiene.

prene and iodoprene, the s-trans, in the cases of the trihalobutadienes, a skew form.

Experimental Section

Bromoprene and Iodoprene. The syntheses of Carothers and Berchet[18] were repeated.[19] The compounds as obtained were 98+ % pure, as judged by vpc, mass spectra, and lack of extraneous peaks in the nmr spectra (Figure 4).

1,1,1,3-Tetrachloro-3-bromobutane (I). Bromotrichloromethane (133 g, 0.67 mol), 2-chloropropene (16.5 g, 0.219 mol), and benzoyl peroxide (3.1 g, 0.013 mol) were heated together at 85° for 5 hr.[20] Excess bromotrichloromethane was removed by distillation. The residue, distilled at 46–48° (0.01 mm), yielded 41.2 g (69%) of I; nmr spectrum: singlet, τ 7.37 (intensity 3); singlet, τ 6.01 (intensity 2).

1,1,3-Trichlorobutadiene (II). A mixture of 60 ml of triethanolamine and 60 ml of water was refluxed in a 200-ml, three-necked flask equipped with a dropping funnel, a mechanical stirrer, and a "water separator." I (22.5 g, 0.082 mol) was dropped into the boiling mixture during a period of 30 min, while the steam-distilled heavy organic layer was constantly separated. The steam distillate, containing about 25% product and much starting material, was fractionated using a small Craig column (bath temperature 70° (20 mm)) to yield 1.59 g (7%) of II (98+% pure mass spectrum, m/e 156, 158, 160, 162, intensities 27:27:9:1; for nmr, see Figure 4).

1,1,1,3,3-Pentabromobutane (III). Tetrabromomethane (200 g, 0.165 mol) and 2-bromopropene (20 g, 0.165 mol) dissolved in 110 ml of carbon tetrachloride were irradiated with a 200-W bulb for 20 hr, with cooling. The carbon tetrachloride was distilled away,

(18) W. H. Carothers and G. J. Berchet. J. Am. Chem. Soc., 55, 2807 (1933).
(19) We are grateful to Dr. R. J. Ferguson for a gift of 4-chlorobutadiene-1,2.
(20) M. S. Kharasch, E. V. Jensen, and W. H. Urry, J. Am. Chem. Soc., 69, 1100 (1947); M. S. Kharasch, O. Reinmuth, and W. H. Urry, ibid., 69, 1105 (1947).
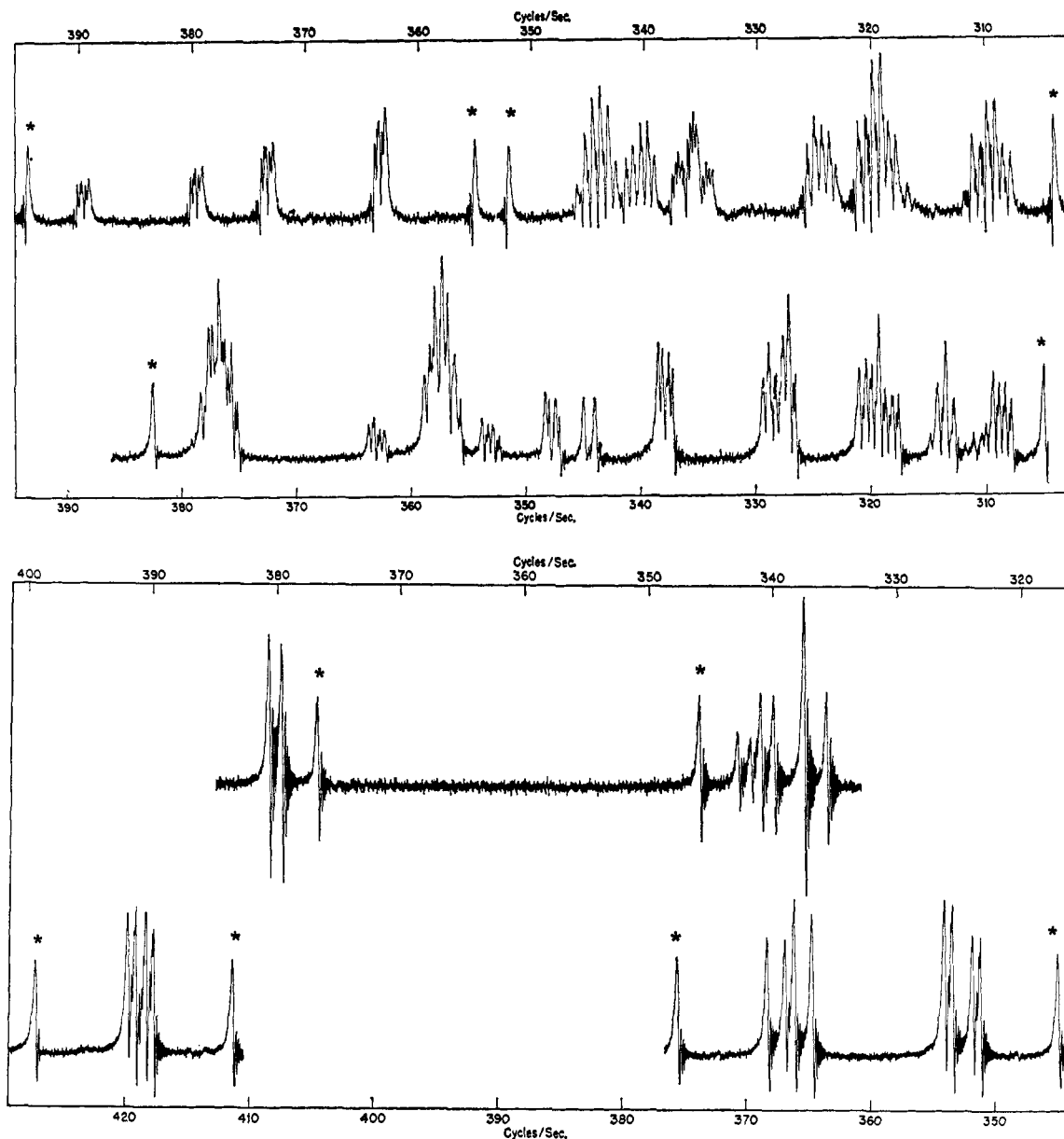
Figure 5. Proton nmr spectra of halogenated butadienes at room temperature: A (top), upper trace, 2-bromobutadiene; lower trace, 2-iodobutadiene; B (bottom), upper trace, 1,1,3-trichlorobutadiene; lower trace, 1,1,3-tribromobutadiene. Asterisk stands for calibration side bands. Upper scale applies to upper trace, lower to lower. Peak positions are in cycles per second (cps) from internal TMS at 60 Mcps.

the tetrabromomethane was removed by sublimation, and the residue was distilled at 97–98° under high vacuum to yield 58.2 g (78%) of III, a colorless oil; nmr: singlet, τ 7.12 (intensity 3); singlet, τ 5.54 (intensity 2).

1,1,3-Tribromobutadiene (IV). The same procedure employed in the preparation of the trichloro compound yielded from 22.7 g of III 1.16 g (8%) of IV, distilled in the Craig column under high vacuum with a bath temperature of 75–85°. In this case the mass spectrum showed the presence of a small amount (about 5%) of dibromochlorobutadiene, presumably the 1,1-dibromo-3-chloro isomer, m/e 288, 290, 296, 294, relative intensities 1:3:3:1, with small peaks at 244, 246, 248, and 250.
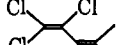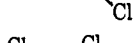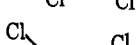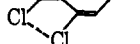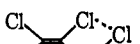
Spectra. Nmr spectra were recorded using a Varian A-60 spectrometer and techniques previously described.[1] Uv spectra were recorded using a Cary Model 14. Mass spectra[21] were obtained on the AEI MS-9.

Results

Uv Spectra. Ultraviolet absorption spectra of the four compounds are reproduced in Figure 5. The λ_{max} and ϵ for these compounds together with selected values from the literature are given in Table I. Since the 1,4-chloro-substituted compounds (entries 5, 6, 7, and 8, Table I) are known[1,7–9] to be planar, it is clear that chlorine substitution on a terminal carbon is alone sufficient to cause λ_{max} to migrate to the 240–265-mμ region. On the other hand high-intensity absorption is associated with the compounds known to be s-trans and low intensity with those known to be in some other conformation (hexachlorobutadiene, entry 16; see also Braude[16]). In general, a fall in intensity is observed when the s-trans form is destabilized by one interaction between chlorine substituents in positions 1 and 3 (indicated by the dotted line—entries 11, 12,

Table I. Ultraviolet Absorption Maxima and Extinction Coefficients of Substituted Butadienes

Compound	λ_{max}, mμ	ϵ	Ref
1	217	20,900	a
2	223	14,100	b
3	222	16,600	c
4	221	12,600	c
5	246	26,100	d
6	243	28,600	d
7	240	32,500	d
8	265	26,400	e
9 (?)	260	23,500	e
10 (?)	248	23,500	e
11 (?)	258	12,600	e
12	264	9,350	e
13	245	8,710	c
14	252	6,310	c
15 (?)	250	5,630	e
16	253	4,470	e

a E. Borello and A. Catino, *Ann. Chim.* (Rome), 46, 571 (1956); API Catalogue of UV Spectral Data, Spectrum No. 65. b K. Bowden, E. A. Braude, and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946). W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* (London), A174, 224 (1940). c This research. d H. G. Viehe and E. Franchimont, *Chem. Ber.*, 97, 602 (1964). e A. Roedig and R. Kloss, *Ann.*, 612, 1 (1958). Question marks: geometrical structure not investigated; see text.

and 13) and a slight further fall when a second interaction between substituents in positions 2 and 4 is introduced (entries 15 and 16). In the table several entries are marked with question marks (9, 10, 11, and 15); in these cases the stereochemistry of the substituents has not been established by chemical means, and the indicated stereochemistries are assigned on the basis of consistency with the above scheme of absorption intensities. The tribromobutadiene (entry 14) also absorbs with low intensity consistent with destabilization of the
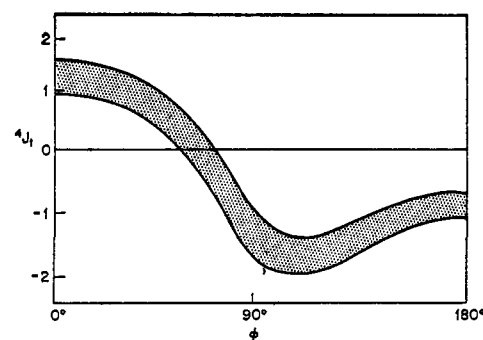
Figure 6. General shape of curve showing dependence of ^4J_t on dihedral angle in butadienes.

s-trans form by the large 1,3-bromine–bromine interaction.

Nmr Spectra. Spectra for the four compounds studied are reproduced in Figure 4. Table II contains the parameters obtained from analysis[22] of the nmr spectra of the compounds at several temperatures. The signs of the coupling constants in the haloprenes are established relative to the ^3J_c and ^3J_t H,H constants by the analysis. In the case of tribromobutadiene, the relative signs of the coupling constants were determined by a frequency-sweep tickling[23] experiment. The negative sign was chosen on the basis of analogy with geminal coupling constants in related compounds.[24] The negative sign was arbitrarily chosen in the case of the trichloro compound. For the sake of comparison, the previously reported data on fluoroprene and chloroprene[25] are reproduced in Table I.

A comparison of the data for the haloprenes at 35° shows no remarkable changes in those coupling constants which might be sensitive to rotation about the central single bond (^3J_s, ^4J_c, ^4J_t, $^5J_{cc}$, $^5J_{ct}$, $^5J_{tt}$) but instead a rather smooth monotonic change in the sequence F, Cl, Br, I. The coupling constant ^4J_t would be expected[1,26] to have values which are near zero or positive in cisoid forms; however in bromoprene and iodoprene they are negative with values close to those for s-trans-butadienes.[1,25] The changes in coupling constants with temperature are monotonic and apparently real, although they are very small and occur in coupling constants between protons within the vinyl group as well as between those separated by the central single bond; the smallness of the changes indicates no great change in rotamer population as a result of temperature variation. Judging from the combined uv and nmr data, it seems highly probable that bromoprene and iodoprene are very largely in the s-trans form.

^4J_t coupling constants in open-chain and cyclic butadienes[26–29] apparently conform to a curve of the general shape shown in Figure 6. In butadienes which are constrained to an s-cis conformation ($\phi = 0°$),

(22) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, 41, 3863 (1964).
(23) R. Freeman and W. A. Anderson, *ibid.*, 37, 2053 (1962).
(24) J. A. Pople and A. A. Bothner-By, *ibid.*, 42, 1339 (1965).
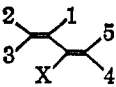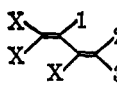(25) A. A. Bothner-By and R. K. Harris. *J. Am. Chem. Soc.*, 87, 3445 (1965).
(26) S. Sternhell, *Rev. Pure Appl. Chem.*, 14, 15 (1964).
(27) A. A. Bothner-By and E. Moser, to be published.
(28) J. D. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *J. Am. Chem. Soc.*, 87, 3896 (1965).
(29) H. Günther and H. H. Hinrichs, private communication.

Table II. Nmr Spectral Data for Haloprenes and 1,1,3-Trihalobutadienes

	X = F[b] T = 35°	X = Cl[b] T = 35°	X = Br[c] T = 35°	X = Br[c] T = -53°	X = I[d] T = +85°	X = I[d] T = 35°	X = I[e] T = -53°
$\nu_1{}^a$	363.66	370.68	374.66	375.33	347.78	347.35	347.37
ν_2	306.96	305.70	315.05	317.46	308.63	315.58	318.75
ν_3	331.02	335.28	334.08	334.36	321.98	322.23	322.04
ν_4	275.58	312.18	336.05	337.91	355.10	357.27	359.28
ν_5	259.14	304.50	344.40	346.72	374.30	376.76	380.18
$^3J_c = J_{12}$	11.14	10.51	10.41	10.34	10.21	10.16	10.00
$^3J_t = J_{13}$	17.32	16.54	16.31	16.25	16.10	16.04	16.00
$^4J_t = J_{14}$	+0.09	-0.18	-0.32	-0.28	-0.58	-0.58	-0.57
$^4J_c = J_{15}$	-0.19	-0.60	-0.76	-0.74	-1.12	-1.08	-1.03
$^2J = J_{23}$	1.24	0.95	0.82	0.83	0.65	0.59	0.53
$^5J_{tt} = J_{24}$	1.44	1.42	1.34	1.38	1.17	1.24	1.30
$^5J_{tc} = J_{25}$	0.73	0.72	0.69	0.71	0.62	0.65	0.66
$^5J_{ct} = J_{34}$	0.62	0.61	0.61	0.61	0.55	0.54	0.53
$^5J_{cc} = J_{35}$	0.70	0.67	0.70	0.71	0.62	0.66	0.67
$^2J = J_{45}$	-2.72	-1.07	-1.35	-1.42	-1.00	-1.04	-1.09

Trihalobutadienes

	X = Cl[f] T = +109°	X = Cl[f] T = +60°	X = Cl[c] T = +35°	X = Cl[c] T = -52°	X = Br[f] T = +109°	X = Br[f] T = +60°	X = Br[c] T = +35°	X = Br[c] T = -53°
ν_1	378.25	378.60	380.01	379.65	419.01	419.26	418.85	418.33
ν_2	338.62	338.95	341.36	345.40	366.26	366.47	366.50	369.76
ν_3	334.12	334.60	337.01	339.83	351.97	352.33	352.87	355.42
$^4J_c = J_{12}$	-1.01	-1.06	-1.05	-1.00	-1.24	-1.42	-1.43	-1.42
$^4J_t = J_{13}$	(0.0)[g]	(0.0)	(0.0)	(0.0)	-0.56	-0.59	-0.60	-0.48
$^2J = J_{23}$	-1.75	-1.76	-1.83	-1.97	-2.14	-2.11	-2.20	-2.39

[a] Chemical shifts in cycles per second (cps) from tetramethylsilane internal standard at 60 Mcps. Coupling constants in cps. [b] Reference 27. [c] 50% (v/v) in CDCl$_3$. [d] 40% (v/v) in cyclohexane, which served as a secondary standard. [e] 40% (v/v) in CDCl$_3$. [f] 67% (v/v) in cyclohexane, which served as a secondary standard. [g] Typical value -0.04 ± 0.06. No splitting directly observable.

^4J_t is positive,[26,28,29] while when $\phi = 180°$, ^4J_t is negative.[1] The point at which the curve crosses the axis is uncertain. In cycloheptatriene, where $\phi = 54°$ as established by electron diffraction measurements,[30] the coupling corresponding to ^4J_t has the value[28] +0.8 cps.

Since ^4J_t for 1,1,3-trichlorobutadiene and 1,1,3-tribromobutadiene has the values 0.0 and -0.6 cps, respectively, it appears that these compounds are not in the s-cis form but in a skew form, with $\phi > 50°$. The more negative value for the tribromobutadiene is consistent with a greater dihedral angle, which in turn is consistent with the greater steric requirements of the bromine in the 1 position.

While the interactions between pairs of substituents

(30) S. Traetteberg, J. Am. Chem. Soc., 86, 4265 (1964).

in the 1,3 position in butadiene (H,H), chloroprene and the 1,4-dichlorobutadienes (H,Cl) do not destabilize the s-trans form sufficiently to cause appreciable population of a second rotameric form, those in 1,1,3-trichloro- and 1,1,3-tribromobutadienes (Cl,Cl and Br,Br) do. This suggests the investigation of butadienes with pairs of substituents of intermediate size, such as F,F or Cl,F. The results of such an investigation are presented in an accompanying paper.