Moeller, *et al.*[4]) were measured between 1.3 and 77.2°K. using the same general method as described by Fritz, *et al.*[5]

The purity of the specimens was 99.9% or better (with respect to content of the rare earth), with the exception of the neodymium chelates, which contained 1% impurity (praseodymium and samarium, both weaker magnetically than the neodymium). Carbon-hydrogen analyses showed in all cases excellent agreement with values calculated for the compositions listed. Measurements were made at four temperatures in the liquid helium range (1 to 4°K.), four in the hydrogen range (10 to 20°K.) and two in the liquid nitrogen range (65 to 77°K.). $CuSO_4 \cdot 5H_2O$ was used for calibration as before.[5] In all cases measurements were made at 400 and 1000 cycles. Agreement of the "dynamic" susceptibilities obtained at these two frequencies was taken to indicate absence of relaxation effects, and the static susceptibility was then taken as the average of the two results. In the case of Dy(acac)$_3 \cdot H_2O$ alone, we observed relaxation at and below 4.2°K.; for this specimen measurements were made also at 100, 200 and 2000 cycles. Even for the lowest susceptibilities obtained, the correction for diamagnetism was estimated to be within the uncertainty of measurement and was not applied.

The data now are being subjected to detailed theoretical treatment following the crystal-field model. Details of the data will be published later, along with the results of the theoretical treatment.

From 1 to 20°K. the data could be fitted by empirical equations of the form of the Curie-Weiss law within about 3% (the precision of the data was about 1%). The constants of these equations are given in Table I, along with the theoretical Curie constants of Van Vleck and Fowler.[6] The large deviations of the empirical "Curie" constants from the high temperature theoretical values indicate mainly that at these low temperatures only some of the low lying multiplets are populated. Some interesting facts become apparent when our results are compared with one another and with earlier measurements on octahydrated sulfates of Pr and Nd,[7] Gd,[8] Dy, Er and Yb.[9,10]

TABLE I

Range °K.	Compound	C (Exptl.)	Δ, °K.	*C* (Van Vleck)
20–1	Pr(acac)$_3 \cdot H_2O$	1.25	11.3	1.64
	Nd(acac)$_3 \cdot H_2O$	1.04	1.1	1.69
	Gd(acac)$_3 \cdot H_2O$	8.0	0.56	7.87
	Tb(acac)$_3 \cdot H_2O$	9.6	0.67	11.81
	Dy(acac)$_3 \cdot H_2O$[a]	15.4	1.54	14.0
	Ho(acac)$_3 \cdot H_2O$	10.4	1.67	14.0
20–4	Er(acac)$_3 \cdot H_2O$	8.3	1.7	11.5
4–1		5.9	0.0	
20–3	Tm(acac)$_3 \cdot H_2O$	6.6	0.0	7.2
3–1		11.9	3.3	
20–1	Yb(acac)$_3 \cdot H_2O$	1.3	0.0	2.53
	Na[Pr(EDTA)]$\cdot 8H_2O$	2.4	0.58	1.64
	Na[Nd(EDTA)]$\cdot 8H_2O$	0.73	0.29	1.69
	Na[Gd(EDTA)]$\cdot 8H_2O$	8.3	0.0	7.87

[a] Below 10°K. the data are for the static (zero-frequency) susceptibility calculated using the Debye model.

For praseodymium and neodymium, the temperature dependence of susceptibility is complicated, but in both cases the acetylacetone chelate has a distinctly larger susceptibility than the EDTA complex, and this in turn larger than the sulfate. For gadolinium, the acetylacetonate, the EDTA complex, and the sulfate are all relatively ideal. For erbium, the only member of the series beyond gadolinium for which detailed information about the sulfate is available, the situation is reversed, with the sulfate showing a larger susceptibility than the acetylacetone. Dysprosium acetylacetonate, with the observed relaxation effects, is obviously a special case; the data available for ytterbium sulfate do not permit detailed comparison with the chelate. It is clear, however, that in all cases the magnetic behavior of the acetylacetone complex is definitely different from that of an ordinary hydrated salt.

The change in properties of the compounds of the elements after gadolinium is also apparent through observations on formation constants of rare earth chelates, where the stabilities of the various compounds fit an electrostatic picture of bonding up to gadolinium but fail to do so thereafter.[2] In view of the complicated multiplet structure of the low-lying spectroscopic states of the rare earth ions, considerable detailed theoretical work will be required for a full explanation of the observed magnetic behavior.

The relaxation phenomena observed for Dy(acac)$_3 \cdot H_2O$ in the helium range could be fitted by a simple Debye model[11] at the low frequency end (400 cycles and below). The relaxation time obtained from this model was about 10^{-3} sec., and decreased with increasing temperature.

[4] T. Moeller, F. A. J. Moss and R. H. Marshall, *J. Am. Chem. Soc.*, **77**, 3182 (1955).

[5] J. J. Fritz, R. V. G. Rao and S. Seki, *J. Phys. Chem.*, **62**, 703 (1958).

[6] See p. 243 of J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, New York, N. Y., 1932.

[7] C. J. Gorter and W. J. DeHaas, *Comm. Phys. Lab., University of Leyden*, No. 218b.

[8] H. Van Dijk, *ibid.*, No. 267_a.

[9] W. J. DeHaas, E. C. Wiersma and W. H. Capel, *ibid.*, *Leyden* No. 201_b.

[10] L. C. Jackson, *Proc. Roy. Soc.* (*London*), **43**, 741 (1939).

[11] See C. G. Gorter, "Paramagnetic Relaxation," Elsevier Publishing Company, Inc., Houston, Texas, 1947.

[12] On leave from University of Lund (Sweden).

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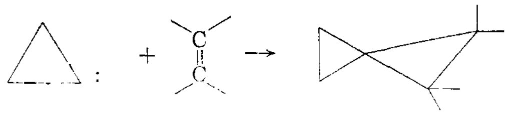
RECEIVED AUGUST 24, 1960

THE CYCLOPROPYL CARBENE

Sir:

The cyclopropyl carbene, a previously unreported species, appeared most intriguing to us for two reasons. First, its addition to olefins should lead to the formation of substituted spiropentanes, a type of compound for which no general method of synthesis is known.[1] Second, it would be of theo-

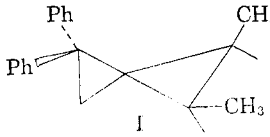
[1] *Cf.* D. E. Applequist, G. F. Fanta and B. W. Henrikson, THIS JOURNAL, **82**, 2368 (1960).



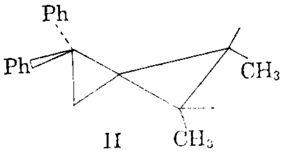
retical interest to determine the paired or unpaired condition of the non-bonding electrons in such a highly strained cyclic system. This could be determined readily by examining the stereochemistry of its reactions with geometrically isomeric olefins.[2]

The 2,2-diphenylcyclopropyl system was selected for this investigation. Known 2,2-diphenylcyclopropanecarboxylic acid[3] was converted *via* its acid chloride to the acid azide. The azide was rearranged to the isocyanate which was converted to the urea, m.p. 134–135°; Found: C, 75.98; H, 6.44; N, 11.07. Nitrosation of the urea gave a surprisingly stable nitrosourea, m.p. 111–111.3° (dec.); found; C, 68.42, H, 5.53, N, 14.88. Treatment of the nitroso compound with a variety of bases effected nearly quantitative evolution of nitrogen. It is interesting that the presumed diazocyclopropane apparently is far less stable than the corresponding diazocyclobutane.[4] Under the mildest possible conditions that would effect reaction of the N-nitrosourea (−5 to 0°) with base, nitrogen evolution was observed. On occasion, transient orange colors were observed, probably resulting from the diazo-material. In the reactions with olefins, the nitrosourea was decomposed with lithium ethoxide. The olefin was used as the solvent. *cis*- and *trans*-2-butene gave, in addition to the anticipated and consistently observed decomposition products of the carbene,[5] different hydrocarbon products which gave correct analyses for the corresponding spiropentanes I (or II) and III.[6] *cis*-2-Butene product, m.p. 31.0–32.0°; found: C, 92.06, H, 7.76, mol. wt., 258. *trans*-2-Butene product, m.p. 51.5–52.0°; found: C, 92.05; H, 7.91; mol. wt., 252.

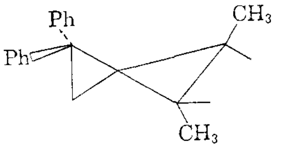
The spiropentane structures were assigned, not only as a result of their analyses and method of preparation, but also as a result of these observed properties. When pure the two products were found to decolorize permanganate very slowly. Neither showed any detectable reaction with bromine in carbon tetrachloride. Their infrared spectra were virtually identical from 3.0 to 8.5 microns. Neither exhibited any absorption between 5.9 and 6.5 microns except for the typical phenyl absorption which appeared at 6.29 microns. Both showed absorptions at 9.86 microns (possibly due to the cyclopropane rings).[7] The major differences in the spectra appeared at 8.76, 12.23, 13.34 (*cis*-absorptions), 9.06 and 10.53 (*trans*-absorptions) microns.



I



II



III

The ultraviolet spectra of the two materials were virtually identical showing weak absorptions (extinction coefficients between 500 and 850) at 255 261, 268 and 276 millimicrons. Both the positions and extinction coefficients of the absorptions are typical of the spectra of several substituted 2,2-diphenylcyclopropanes that we have examined.

Further evidence for the spiropentane structures was obtained by examination of the n.m.r. spectra of the two compounds. Whereas the spectrum (60 mc.) of the material resulting from reaction with *trans*-2-butene showed two peaks at −0.712 and −0.53 p.p.m. (from benzene), the product from *cis*-2-butene exhibited a single peak at −0.64 p.p.m. Furthermore, both materials showed non-equivalence quartets centering at about 5.0 p.p.m. (*trans*-4.97 p.p.m. and *cis*-5.08 p.p.m.) which were assigned to the two hydrogens *beta*- to the two phenyl rings. The shift of the position of these peaks from the position of the CH_2 peak in spiropentane[1] (5.76 p.p.m.) is consistent with the shifts which we have observed resulting from the substitution of two phenyls on one carbon of substituted cyclopropanes. Finally, the areas of these two peaks as compared with the total area of the non-aromatic hydrogens corresponded to 2.1 and 1.9 hydrogens for the *trans*- and *cis*- materials, respectively. The other non-aromatic hydrogen peaks appeared in the range of 5.3 to 5.5 p.p.m.

Examination of the infrared spectra of the hexane soluble crude reaction mixtures indicated that both of the reactions were, within detectable error, completely stereospecific. Analyses of the crude reaction mixtures employing gas chromatography were not completely satisfactory. However, it was possible to confirm the absence of any of the *cis*-product (or products) in the mixture resulting from the reaction of the carbene with *trans*-2-butene. Contaminants and curve shapes prevented similar conclusions in the other case but did show unequivocally that the crude reaction mixture contained predominantly the *cis*-product.

These observations indicate that, at the moment of reaction, the cyclopropyl carbene exists in the singlet state. In addition, we have presented a potentially general method for the syntheses of the rather elusive[1] substituted spiropentanes.

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[2] R. C. Woodworth and P. S. Skell, This Journal, **81**, 3383 (1959); P. S. Skell and J. Klebe, *ibid.*, **82**, 247 (1960); F. A. L. Anet, R. F. W. Bader and A. M. Van der Auwera, *ibid.*, **82**, 3217 (1960), and references cited in these papers.

[3] Prepared from diphenyldiazomethane by the procedure of H. M. Walborsky and F. M. Hornyak, *ibid.*, **77**, 6026 (1955).

[4] D. E. Applequist and D. E. McGreer, *ibid.*, **82**, 1965 (1960).

[5] The decomposition products of the cyclopropyl carbene will be discussed in a forthcoming publication.

[6] Although the structure of the product arising from *trans*-2-butene can be safely assigned structure III, we have no evidence at present that will allow a distinction between I and II for the crystalline product isolated from the reaction with *cis*-2-butene; nor can it be stated unequivocally that the crude reaction product did not contain both isomers. Since the isolated material was certainly the predominant spiropentane, steric considerations lead us to favor II as the more likely structure.

[7] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 28.

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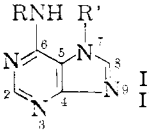
RECEIVED AUGUST 30, 1960

THE STRUCTURE OF TRIACANTHINE[1]

Sir:

Early reports suggested the presence of alkaloidal material in species of *Gleditsia*,[2,3] of the Leguminosae family, and recently the alkaloid "triacanthine" has been isolated from *Gleditsia triacanthos* L. and the formula $C_8H_{10}N_4$ assigned.[4] We have repeated the described extraction procedure on the young leaves of *G. triacanthos* collected by one of us (J.A.D.) in April at Dixon Springs, Illinois,[5] and have established that the correct molecular formula for triacanthine is $C_{10}H_{13}N_5$ and that the structure is 6-amino-7-(γ,γ-dimethylallyl)-purine (I).



I, R = H, R' = $CH_2CH{=}C(CH_3)_2$
II, R = H, R' = H
III, R = $CH_2C_6H_5$, R' = $CH_2CH{=}C(CH_3)_2$
IV, R = H, R' = $CH_2CH_2CH(CH_3)_2$

Analytical data for triacanthine, m.p. 228–229° (reported[4] 227–228°) (Calcd. for $C_{10}H_{13}N_5$: C, 59.09; H, 6.45; N, 34.46. Found: C, 59.29; H, 6.32; N, 34.59), and triacanthine hydrochloride, m.p. 218–220° dec. (reported[4] 218–219°) (Calcd. for $C_{10}H_{14}ClN_5$: C, 50.09; H, 5.89; N, 29.22. Found: C, 50.24; H, 6.04; N, 28.96), as well as the molecular weight determined by electrometric titration[6] (Calcd. for $C_{10}H_{13}N_5$: 203. Found: 211 ± 10; pK'_a 5.4) supported the formula $C_{10}H_{13}N_5$. Triacanthine showed $\lambda_{\max}^{\text{EtOH}}$ (neutral) 273 mμ (ϵ 12,500) and $\lambda_{\max}^{\text{EtOH}}$ (pH 1) 277 (18,300). The mass spectrum of triacanthine[7] showed peaks at mass 203 (confirming the molecular weight), 188 (establishing the presence of at least one methyl group), and 135. Chemical realization of the cleavage suggested by the 135 mass peak was achieved by treatment of triacanthine with concentrated hydrochloric acid at 80° for 8 hours, which produced crystalline adenine (II) hydrochloride, m.p. 283–284° (reported[8] 285–286°). The indentification was made by analysis (Calcd. for $C_5H_6ClN_5{\cdot}0.5H_2O$: C, 33.25; H, 3.91; N, 38.79. Found: C, 33.38; H, 4.01; N, 38.62) and ultraviolet spectrum.[9] A picrate (m.p. 190–192°) formed from the hydrochloride failed to depress the melting point of authentic adenine picrate.[8]

Reaction of triacanthine with benzylamine and benzylamine hydrochloride in a sealed tube at 180° for 12 hours yielded the "exchange amination"[10] product N-benzyltriacanthine (III), m.p. 150° (Calcd. for $C_{17}H_{19}N_5$: C, 69.60; H, 6.53; N, 23.88; mol. wt., 293. Found: C, 69.34; H, 6.52; N, 24.06; electrometric titration mol. wt.,[6] 310 ± 10), $\lambda_{\max}^{\text{EtOH}}$ (neutral) 292 mμ (ϵ 17,100) and $\lambda_{\max}^{\text{EtOH}}$ (pH 1) 287 (24,300). The formation of this product demonstrated that the amino group of adenine is unsubstituted in triacanthine. An n.m.r. spectrum ($CDCl_3$) of N-benzyltriacanthine showed peaks at τ = 2.05 and 2.23,[11] which must derive from the ring hydrogens of adenine.[12] Thus, triacanthine must be represented by adenine substituted only at position 7 or 9. The choice between these two alternatives is made readily in favor of position 7 by studying representative 7- and 9-substituted 6-aminopurines.[9,13] For example, adenosine (9-β-D-ribofuranosidoadenine) shows $\lambda_{\max}^{\text{EtOH}}$ (pH 13) 260 mμ (ϵ 14,300) and $\lambda_{\max}^{\text{EtOH}}$ (pH 1) 260 (14,200) while 7-D-ribofuranosidoadenine shows $\lambda_{\max}^{\text{EtOH}}$ (pH 13) 271 (9,800) and $\lambda_{\max}^{\text{EtOH}}$ (pH 1) 273 (13,600).[13] The n.m.r. spectrum of N-benzyltriacanthine allowed an accurate determination of the number of methyl groups in triacanthine. By using the area of the 2.77 τ peak representing the five phenyl hydrogens as an internal standard, in comparison to the area of the singlet CH_3-C peak at 8.14 τ (after extrapolating to zero rf. power),[14] it was established that there were two C-CH_3 groups present in triacanthine (a Kuhn-Roth C-methyl determination on triacanthine gave a value of 5.73 (calcd. for two C-CH_3 groups, 14.80)). In addition, the τ value for the C-CH_3 peak indicated that the methyl groups are attached to an olefinic carbon atom.[15]

Catalytic reduction of triacanthine with hydrogen and platinum in glacial acetic acid yielded dihydrotriacanthine (IV), m.p. 230-231° (strongly depressed when mixed with triacanthine) (Calcd. for $C_{10}H_{15}N_5$: C, 58.51; H, 7.37. Found: C, 58.55; H, 7.17.), $\lambda_{\max}^{\text{EtOH}}$ (neutral) 273 (13,020) and $\lambda_{\max}^{\text{EtOH}}$ (pH 1) 277 (18,950). In addition to dihydrotriacanthine, a considerable amount of adenine was produced by hydrogenolysis.[16] The

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[1] This investigation was supported by a research grant (USPHS-RG5829) from the National Institutes of Health, U. S. Public Health Service.

[2] C. Wehmer, "Die Pflanzenstoffe," Verlag von Gustav Fischer, Jena, 1929, p. 508.

[3] M. Greshoff, "Mededeelingen uit 's Lands Plantentuin," **29**, 67 (1900), G. Kolff and Co., Batavia, 1900.

[4] A. S. Belikov, A. I. Bankowsky and M. V. Tsarev, *Zhur. Obshcheĭ Khim.*, **24**, 919 (1954).

[5] We wish to record our special thanks to Professors W. R. Boggess and A. R. Gilmore of the Department of Forestry, University of Illinois, for helping us to obtain the leaf material.

[6] We are grateful to Dr. Harold Boaz of Eli Lilly and Company, Indianapolis, Indiana, for this information.

[7] Determined by Dr. Klaus Biemann of the Massachusetts Institute of Technology, to whom we are pleased to acknowledge our thanks.

[8] H. R. Bentley, K. G. Cunningham and F. S. Spring, *J. Chem. Soc.*, 2301 (1951).

[9] J. M. Gulland and E. R. Holiday, *ibid.*, 765 (1936).

[10] C. W. Whitehead and J. J. Traverso, THIS JOURNAL, **82**, 3971 (1960). We are grateful to these authors for providing an advance copy of their article.

[11] G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

[12] C. D. Jardetzky and O. Jardetzky, THIS JOURNAL, **82**, 222 (1960).

[13] W. Friedrich and K. Bernhauer, *Chem. Ber.*, **89**, 2507 (1956).

[14] *Cf.*, J. Pople, W. Schneider and H. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p. 77.

[15] G. V. D. Tiers "Table of τ Values for a Variety of Organic Compounds," Minnesota Mining and Manufacturing Company, St. Paul, Minn., 1958.

[16] Triacanthine is not cleaved by acetic acid under the room temperature conditions of the hydrogenation.