The Dipole Moments and Structure of Cyclic Compounds: Lactones, Lactams, Anhydrides, Carbonates, Carbamates, Ureides, and Imides

CALVIN M. LEE[1] AND W. D. KUMLER

Department of Pharmaceutical Chemistry, School of Pharmacy,
University of California, San Francisco Medical Center,
San Francisco, California

Received April 30, 1962

The dipole moments of cyclohexane-1,3- and 1,4-lactone, cyclohexane-1,3-carbonate, and 1,3-ureide were measured to complete a series of moments of imides,[2-3] lactams,[4] and carbamates.[5] Comparisons between the $-\overset{\mathrm{H}}{\mathrm{N}}-$ and —O— analog and within groups between five- and six-membered ring compounds are given.

Results and Discussion

Table I gives the results of the measurements and Table II lists the dipole moments for related compounds. With one exception, the six-membered ring compounds have higher moments than the five-membered ring compounds. Two reasons for this were discussed in previous papers,[1,4] namely, the larger angles between the main dipoles in the five-membered ring compounds and the opposition of the N^+O^- dipoles to the carbonyl resultant in these compounds.

The difference between the dipole of the five- and the six-membered ring compounds is greatest in the case of anhydrides and imides, being around 1.1 D.; it is about 0.4 D. for carbonates, about 0.3 D. for lactams and ureides, and about 0.1 D. for lactones and carbamates. The larger values for anhydrides and imides as compared with the other five types of compounds is due to the fact that carbonyl groups have higher dipoles than ether, N–H, or N–C groups, so the difference in angle has a larger over-all effect. Another reason the difference is less in case of carbonates, carbamates, ureides, lactones, and lactams is that in these compounds the dipoles in the forms with a separation of charge augment the main carbonyl moment and they do it more in the five-membered ring compounds because the angle is more acute.

Lactones have higher moments than lactams and this does not result from a greater contribution of the forms with a separation of charge, for the carbonyl stretching frequencies are greater in lactones, indicating the C=O in these compounds has more double bond character and, therefore, less contribution from resonance forms with a separation of charge.

Cyclohexane-1,3	Infrared C=O in cm.$^{-1}$ (KBr)
Lactone	1767
Lactam	1669
Cyclohexane-1,4	
Lactone	1730
Lactam	1669

TABLE I
DIPOLE MOMENTS IN DIOXANE AT 30°

Cyclohexane-1,3-lactone

	ω_{12}	ϵ_{12}	ν_{12}
	0.00		
	.0007332	2.22784	0.97427
	.0010766	2.23341	.97417
$\mu = 4.37 \pm 0.04$ D.	.0026900	2.26499	.97377
	.0032037	2.27278	.97362
	.0041664	2.29204	.97347

$\epsilon = 2.21376$ $\nu_1 = 0.97442$ $P_{2_0} = 415.05$ Mol. wt. =
$\alpha = 18.72711$ $\beta = -0.23851$ $P_E = 32.23$ calcd. 126.16

Cyclohexane-1,4-lactone

	ω_{12}	ϵ_{12}	ν_{12}
	0.00	2.20961	0.97442
	.0009112	2.22741	.97417
	.0018368	2.24633	.97397
$\mu = 4.50 \pm 0.03$ D.	.0023417	2.25592	.97377
	.0029836	2.26996	.97367
	.0036619	2.28237	.97357
	.0043407	2.29453	.97347

$\epsilon_1 = 2.20969$ $\nu_1 = 0.97439$ $P_{2_0} = 438.70$ Mol. wt. =
$\alpha = 19.78195$ $\beta = -0.22847$ $P_E = 32.23$ calcd. 126.16

Cyclohexane-1,3-carbonate

	ω_{12}	ϵ_{12}	ν_{12}
	0.00	2.21996	0.97391
	.004128	2.21475	.97385
	.0009413	2.22904	.97381
$\mu = 6.14 \pm 0.03$ D.	.0026349	2.28408	.97371
	.0037361	2.32012	.97357
	.0040934	2.33133	.97347

$\epsilon_1 = 2.20001$ $\nu_1 = 0.97391$ $P_{2_0} = 790.54$ Mol. wt. =
$\alpha = 32.05873$ $\beta = -0.09527$ $P_E = 34.02$ calcd. 142.16

Cyclohexane-1,3-ureide

	ω_{12}	ϵ_{12}	ν_{12}
	0.00	2.20353	0.97357
	.0003070	2.20825	.97328
	.0006980	2.21200	.97308
$\mu = 3.69 \pm 0.05$ D.	.0020344	2.22896	.97308
	.0021452	2.22972	...

$\epsilon_1 = 2.20402$ $\nu_1 = 0.97336$ $P_{2_0} = 311.03$ Mol. wt. =
$\alpha = 12.26629$ $\beta = -0.30312$ $P_E = 37.66$ calcd. 140.19

This higher moment of lactones is due to the ether moment being in a direction which augments the carbonyl moment, while in lactams the —NH moment to some extent opposes the carbonyl moment.

Carbonates have higher moments than ureides and the same reasons apply here. The infrared shows that the carbonates have higher carbonyl frequencies than the ureides,

Cyclohexane-1,3-carbonate	1724 cm.$^{-1}$
Cyclohexane-1,3-ureide	1669 cm.$^{-1}$

so there is more resonance and contribution of forms with a separation of charge in the ureides but the other effects mentioned above overcome this and the higher moments for carbonates result.

---

[1] Present address: School of Pharmacy, Chelsea College of Science and Technology, Chelsea, London. Requests for reprints should be addressed to W. D. Kumler at San Francisco.

[2] (a) C. M. Lee and W. D. Kumler, *J. Am. Chem. Soc.*, **83**, 4586 (1961); (b) C. M. Lee and W. D. Kumler, *ibid.*, **84**, 565 (1962).

[3] C. M. Lee and W. D. Kumler, *ibid.*, **84**, 571 (1962).

[4] C. M. Lee and W. D. Kumler, *ibid.*, **83**, 4593 (1961).

[5] C. M. Lee and W. D. Kumler, *ibid.*, **83**, 4596 (1961).

TABLE II

	Anhydride	Lactone	Carbonate	Carbamate	Lactam	Ureide	Imide
5-membered	Succinic 4.22^a	Butyro 4.09^b	Ethylene 4.80^c	Ethylene 5.07^d	Butyro 3.55^f	Ethylene 3.94^h	Succinic 1.47^i
6-membered	Glutaric 5.31^e	Valero 4.22^b	Trimethylene 5.21^c	Trimethylene 5.10^d	Valero 3.83^f	Trimethylene 4.22^h	Glutaric 2.58^i
6-membered	Cyclohexane-1,3 4.97^e	Cyclohexane-1,3 4.37	Cyclohexane-1,3 6.14	Cyclohexane-1,3 5.64^d	Cyclohexane-1,3 3.73^g	Cyclohexane-1,3 3.69	Cyclohexane-1,3 2.89^i
		Cyclohexane-1,4 4.50		Cyclohexane-1,4 5.60^d	Cyclohexane-1,4 4.24^g		

[a] G. Rau and N. Ansatanarayanan, *Proc. Indian Acad. Sci.*, **5A**, 185 (1937). [b] Benzene, 25°; R, Huisgen and H. Ott, *Tetrahedron*, 6 253 (1959). [c] Benzene, 25°; R. P. Steward and E. C. Vierira, *J. Chem. Phys.*, **62**, 127 (1958). [d] C. M. Lee and W. D. Kumler, *J. Am. Chem. Soc.*, **83**, 4596 (1961). [e] C. M. Lee and W. D. Kumler, *J. Org. Chem.*, **27**, 2055 (1962). [f] Benzene, 25°; R. Huisgen and H. Walz, *Chem. Ber.*, **89**, 2616 (1956). [g] C. M. Lee and W. D. Kumler, *J. Am. Chem. Soc.*, **83**, 4593 (1961). [h] Unpublished data; Brian Loader, L. E. Sutton, and W. D. Kumler. [i] C. M. Lee and W. D. Kumler, *J. Am. Chem. Soc.*, **83**, 4586 (1961).

Anhydrides have higher moments than imides and here the same factors will be operating.

Compounds with nitrogen in the ring, namely, the imides, ureides, and lactams occupy the seventh, sixth, and fifth positions.

Five membered:
carbamate > carbonate > anhydride > lactone > ureide > lactam > imide

Six membered:
anhydride > carbonate > carbamate > lactone > ureide > lactam > imide

Six membered, 1,3-bridge:
carbonate > carbamate > anhydride > lactone > lactam > ureide > imide

Lactones are always in the fourth position with anhydrides third or first and carbonate second or first. Thus, in general, the compounds with oxygen in the ring have higher moments than those with nitrogen. The carbamate with both oxygen and nitrogen in the ring might be expected to be intermediate, but actually is near the front of the order being first, second, and third. The reason for this probably is that most of the plus charge in the forms with a separation of charge is confined to the nitrogen which augments the resultant of the ether and the carbonyl dipoles, giving rise to a high moment.

Experimental

All dipole moments were measured in dioxane at 30° and calculations were made using the equation and method of Halverstadt and Kumler.[6]

Acknowledgment.—We wish to thank Dr. H. K. Hall, Jr., of DuPont for providing the compounds.[7] We also wish to thank Mr. M. K. Hrenoff of the Spectrographic Laboratory for all spectrographic measurements. Infrared spectra were run on Perkin-Elmer, Model 21.

---

(6) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

(7) H. K. Hall, Jr., M. K. Brandt, and R. M. Mason, *ibid.*, **80**, 6412 (1958).

Diels–Alder Adducts of Hexachlorocyclopentadiene with Mono- and Divinyl Substituted Benzenes

CARLETON W. ROBERTS AND DANIEL H. HAIGH

Polymer Research Laboratory, The Dow Chemical Company, Midland, Michigan

Received August 13, 1962

During the course of investigations aimed at developing a relationship between the structure and fire retardancy of halogen-containing compounds in polymeric systems, it was necessary to prepare several examples of the products derived from hexachlorocyclopentadiene by the Diels–Alder reactions with mono- and divinyl derivatives of substituted benzenes. This report describes the preparation of some of these compounds[1,2]; their use in polymeric systems is described in a previous publication.[3]

The Diels–Alder reaction proceeded with considerable ease in each of the cases studied; it was found that the styrene adduct previously described[4,5] is dimorphic. The reaction of commercial divinylbenzene with hexachlorocyclopentadiene gave rise to the two bis-adducts expected from the analysis of the starting isomeric divinylbenzenes. In addition, the commercial material contained isomeric ethylstyrenes, and from the bis-adduct reaction mixtures it was also possible to isolate the mixture of isomeric adducts of the ethylstyrenes. The pure bis-adduct from 1,2-divinylbenzene was prepared to determine the steric requirements imposed by the presence of two "norbornenyl" groups *ortho* to each other on the benzene ring. The yield of product indicates that the formation of the *ortho* product is not severely hindered.

---

(1) C. W. Roberts, U. S. Patent 2,952,711 (September 13, 1960).

(2) C. W. Roberts and D. H. Haigh, U. S. Patent 2,952,712 (September 13, 1960).

(3) C. W. Roberts, U. S. Patent 2,976,842 (January 10, 1961).

(4) P. B. Polen, M. Kleiman, and H. G. Fechter, U. S. Patent 2,673,172 (March 23, 1954).

(5) S. H. Herzfeld, R. E. Lidov, and H. Bluestone, U. S. Patent 2,606,910 (August 12, 1952).