for comparing their alkaloid sample with authentic maritidine.

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1. Manske, R. H. F., *The Alkaloids*, Academic Press, London, 1960, 6, 397.
2. Krishna Rao, R. V., *Indian J. Pharm.*, 1969, 31, 62.
3. —, *Ibid.*, 1969, 31, 86.
4. Sandberg, F. and Michel, K.-H., *Lloydia*, 1963, 26, 78.
5. Manske, R. H. F., *The Alkaloids*, Academic Prses, London, 1968, 11, 356.

PHYSICOCHEMICAL INVESTIGATION OF RARE-EARTH CHELATES OF 2-(N-2-HYDROXY BENZYLIDINEIMINO) ETHANE SULPHONIC ACID

A PERUSAL of the literature[1-2] has revealed that no work has been done on the rare-earth chelates of 2-(N-2-hydroxy benzylidineimino) ethane sulphonic acid (H_2BE). The physicochemical investigation of the rare-earth-H_2BE chelates have been carried out using potentiometric, magnetic and spectral techniques.

2-(N-2-hydroxybenzylidineimino) ethane sulphonic acid (H_2BE) was synthesised from salicylaldehyde and taurine by the procedure already reported[3].

Potentiometric titrations of mixtures containing (A) perchloric acid alone, (B) perchloric acid and the ligand (H_2BE) and (C) perchloric acid, ligand and metal-ion solution have been carried out by the method of Irving and Rossotti[4].

Mean values of dissociation constants ($\log K_1^H$ and $\log K_2^H$) as obtained by the method of interpolation at half $\bar{n}$ values[5] and interpolation at various $\bar{n}$ values method, have been found to be 10·05 and 8·35 at 25°, 9·81 and 8·09 at 35°, and 9·67 and 7·84 at 45°, respectively. The formation curves for the metal-ligand system attain maxima at $\bar{n} > 1\cdot5$ which indicate that 1:1 and 1:2 chelates are formed. The stability values of the metal chelates were refined by various computational methods[6]. The values obtained by different methods were found in agreement and their average values are summarised in Table I. Thus the stability of the chelates increases with decreasing ionic size of the metal ions, *i.e.*, La(III) < Ce(III) < Pr(III) < Nd(III) < Sm(III) < Gd(III) < Tb(III) < Dy(III) < Ho(III). The values of the free energy change ($\triangle G$), enthalpy change ($\triangle H$) and entropy change ($\triangle S$) of the metal chelates have also been included in Table I.

TABLE I

Molecular weight, average stability, thermodynamic parameters and magnetic moments of rare-earth chelates of H_2BE

Metal chelates	Mol. wt. Calc. (Found)	Stability constants log K_1 log K_2	$-\triangle G$ K. cal/mole	$\triangle H$ K. cal/mole at 35°	$\triangle S$ Cal/deg/ole	μ_{eff} B.M. 308°
[LaL₂]	579 (561)	5·65 (5·74) 6·79* 4·50 (4·55) 4·60*	14·07 (14·51) 16·57*	21·50	116·7	diamagnetic
[CeL₂]	580 (565)	6·05 (6·77) 7·18* 4·63 (5·00) 5·05*	14·72 (16·59) 17·76*	25·52	136·8	2·28
[PrL₂]	581 (567)	6·59 (7·16) 7·50* 4·73 (5·28) 5·30*	15·62 (17·54) 18·56*	23·84	134·4	3·37
[NdL₂]	584 (572)	7·06 (7·42) 7·94* 4·99 (5·65) 5·75*	16·63 (18·42) 19·92*	27·35	148·6	3·66
[SmL₂]	590 (580)	7·62 (7·83) 8·02* 5·26 (5·75) 5·81*	17·77 (19·14) 20·13*	20·60	129·0	1·45
[GdL₂]	597 (582)	8·03 (8·13) 8·61* 5·79 (6·24) 6·29*	14·06 (20·25) 21·68*	21·52	136·2	7·84
[TbL₂]	598 (579)	8·39 (8·42) 8·88* 6·05 (6·62) 6·80*	19·92 (21·19) 22·80*	17·49	125·9	9·51
[DyL₂]	602 (592)	8·51 (8·65) 9·29* 6·40 (6·94) 7·07*	20·57 (12·98) 23·81*	14·95	119·9	10·43
[HoL₂]	605 (595)	8·80 (8·93) 9·54* 7·00 (7·28) 7·40*	21·80 (22·85) 24·65*	19·02	135·9	10·42

The values in parenthesis are at 35° and those with asterisk mark are at 45° C; and $L_2 = C_{18}H_{19}N_2O_8S_2$.

The more negative values of $\angle$ G at 45° than at 35° or 25° and the positive values of $\triangle$H in all the cases suggest that in the chelates steric strain exists around the rare-earth metal ion due to the presence of fused rings. The positive values of $\triangle$S indicate that the entropy term is favourable for their formation.

Solid-chelates: The rare-earth chelates of H_2BE were prepared in the solid state by the method reported earlier[3] and the yields were found between 75–80%. Their molecular weights were determined ebulliometrically (Table I) and 1:2 (metal-ligand) stoichiometry was observed in these compounds.

Lanthanum chelate was found diamagnetic whereas the rest paramagnetic as shown in Table I. From the magnetic moments which are very close to spin-only values, it is apparent that in these compounds there is no metal-metal bonding and, hence, no spin-exchange occurs and they exist as monomers.

The results of I.R. studies are shown in Table II. Based on the data of this investigation, an octahedral stereochemistry of these compounds is suggested.

TABLE II

I.R. spectra of H_2BE and its rare-earth chelates

(in cm^{-1})

Compound	ν (SO$_3$H)	ν (C=N)	ν (OH)	ν (M−O)	ν (M−N)
H_2BE	1170	1630	3600	..	..
Rare-earth-H_2BE chelates	..	1610	..	650–630	600–580

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1. Holm, R. H., Averett (Jr.), G. W. and Chakravorty, A., *Prog. Inorg. Chem.*, 1966, 6, 88.
2. Hodgson, D. I., *Ibid.*, 1975, 19, 1.
3. Ozha, D. D., Singhvi, B. R. and Mehta, R. K., *Acta Chim.*, 1976, 18, 362.
4. Irving, H. and Rossotti, H. S., *J Chem. Soc.*, 1945, p. 2904.
5. Bjerrum, J., *Metal Ammine Formation in Aqueous Solution*, P. Haase and Sons, Copenhagen, 1957, pp. 20, 114, 14 (*a*), 36 (*b*).
6. Irving, H. and Rossotti, H. S., *J. Chem. Soc.*, 1953, p. 3397.

DECARBOXYLATION OF 4-ACETYL-3-ARYL PENT-2-ENE-1, 5-DIOIC ANHYDRIDE. FORMATION OF OXIN-2-ONES

THE condensation product of 3-aryl pent-2-ene-1, 5-dioic acids and fused sodium acetate-acetic anhydride, assigned structure *1* by Bhave and Nerurkar[1], was reported to decarboxylate on heating above its m.p. or on treatment with mineral acid to the lactone *2*.

The structure of the condensation product has been established by us on the basis of spectral studies to be a C-aiylated product 3^2. It is now the contention of the author that the decarboxylation observed by Bhave and Nerurkar proceeds by a retero Diels-Alder fragmentation of the anhydride ring of *3* to give the intermediate ketene *5*, which would readily undergo cyclization to form the 4-aryl-6-methyl oxin-2-one *6*. The structure of the lactone, thus became a moot problem. In the ir spectrum the strong band at 1700 cm^{-1} is most certainly due to the C = O stretching vibrations. The 1650, 1600 cm^{-1} bands are associated with C = C stretching vibrations of the diene system. The nmr spectrum exhibited a three proton singlet, at 2·33 which is due to the methyl protons *d*, the other three proton singlet at 3·88 must be associated with the methoxyl protons *a*.

1

2

3

4

6

5
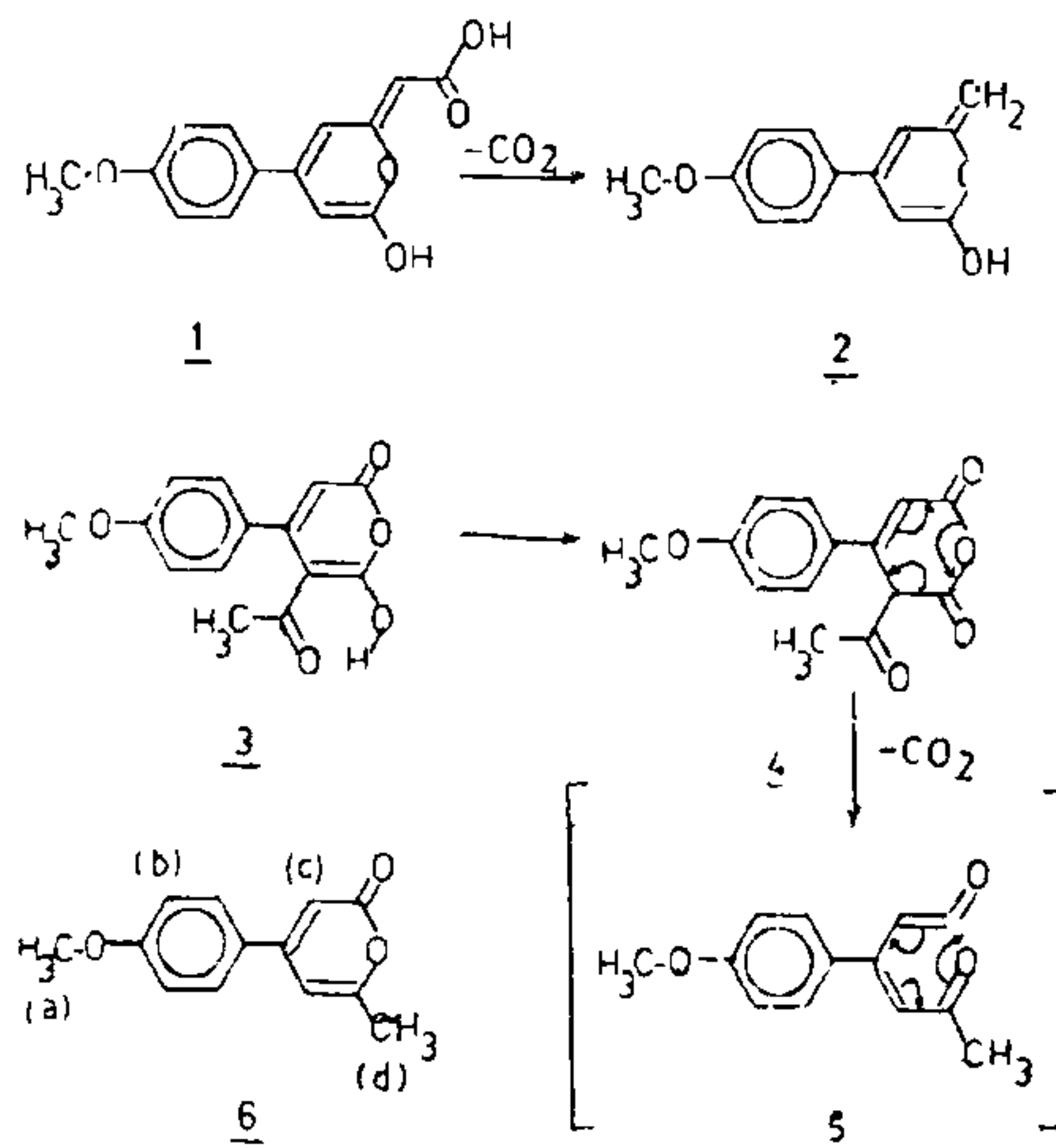
The olefinic proton, *c* resonates at 6·3, and the 'quartet'—two sets of doublets centered at 7·0 and 7·85,—with additional weak lines surrounding the four main signals is evidently that of a *p*-disubstituted benzene. The spectral data, thus clearly substantiates our postulation for the structure and formation of the 4-aryl-6-methyl oxin-2-one.