

On Kinematic Coupling in Dicyclopentadienides

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Kinematic couplings in transition metal sandwich compounds were first discovered by a total normal coordinate analysis of dibenzenechromium¹ and subsequently established for other benzene sandwiches² and for ferrocene.³ In ferrocene, coupling was observed between some framework and some non-planar cyclopentadienide vibrations.³ Since similar phenomena were to be expected for other dicyclopentadienides, we have made a total normal coordinate analysis for the complexes of Ru, Os, V, Cr, Mn, Co, Ni, Mg, Ca, Sr, Ba, and Zn (using the same force field, the same symmetry coordinates and the same structural parameters as in the ferrocene³ analysis).

Main point of interest in this context is the No. 9 non-planar C—H deformation (A_1'') frequency of these compounds. It is

found at 818 cm⁻¹ in the ferrocene spectrum⁴ and corresponds to the 710 cm⁻¹ band of free (ionic) cyclopentadienide. Table 1 gives the values calculated for this frequency with the free C₅H₅⁻ constant, replacing Fe in Fe(C₅H₅)₂ by the masses of the atoms listed above. Comparing these results to the experimental values it is noted that, in all cases, coupling is predicted in the right direction. In contrast to a similar study of a series of benzene-transition-metal complexes,² however, it is seen that the deviations between the experimental and calculated values can be much larger. Apart from a possible influence of changing structural parameters disregarded in our calculations, the observed fluctuations reflect very well the different types of the dicyclopentadienides inspected. It appears that coupling is strong for the more covalent compounds (Fe, Ru, Os), and it is weak for the more ionic molecules (Ca, Sr, Ba, *e.g.*). A similar result is obtained for the other non-planar ligand vibrations (A_1' , E_1' and E_1'') of these compounds.

The mentioned difference in the metal-carbon bond type of the molecules at hand is also apparent if, using the ferrocene force field, some of their framework vibrations are calculated (results for Nos. 11 and 21 in Table 1). The results show satisfying agreement with the experimental values only for ferrocene, ruthenocene and osmocene. In all the other cases the values

Table 1. Comparison of the experimental and the changed calculated frequencies (cm⁻¹) 9, 11, and 21,⁴ when Fe of Fe(C₅H₅)₂ is replaced by different masses (geometrical parameters and force field unchanged). Exp. values taken from Ref. 5.

| Frequency No. | 9 | | 21 | | 11 | |
|---|------|-------|------|-------|------|-------|
| | obs. | calc. | obs. | calc. | obs. | calc. |
| C ₅ H ₅ | 710 | 710 | — | — | — | — |
| Fe(C ₅ H ₅) ₂ | 818 | 818 | 490 | 490 | 477 | 477 |
| Ru(C ₅ H ₅) ₂ | 811 | 810 | 446 | 408 | 379 | 399 |
| Os(C ₅ H ₅) ₂ | 823 | 806 | 428 | 351 | 353 | 344 |
| V(C ₅ H ₅) ₂ | 774 | 820 | 422 | 506 | 379 | 492 |
| Cr(C ₅ H ₅) ₂ | 766 | 820 | 429 | 502 | 408 | 488 |
| Mn(C ₅ H ₅) ₂ | 762 | 818 | — | 493 | — | 480 |
| Co(C ₅ H ₅) ₂ | 778 | 817 | 464 | 481 | 355 | 469 |
| Ni(C ₅ H ₅) ₂ | 772 | 817 | 355 | 482 | — | 469 |
| Mg(C ₅ H ₅) ₂ | 779 | 861 | — | 664 | — | 626 |
| Ca(C ₅ H ₅) ₂ | 760 | 828 | — | 551 | — | 532 |
| Sr(C ₅ H ₅) ₂ | 755 | 811 | — | 425 | — | 416 |
| Ba(C ₅ H ₅) ₂ | 736 | 807 | — | 377 | — | 370 |
| Zn(C ₅ H ₅) ₂ | 760 | 815 | 345 | 465 | — | 454 |

to be expected by the ferrocene force field deviate grossly from the experimental values. This is in marked contrast to a similar study of a series of benzene sandwich compounds.³ These calculations, which used the $\text{Cr}(\text{C}_6\text{H}_6)_2$ force field, reproduced very well the qualitative appearance of the pattern of such framework vibrations in different compounds.

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1. Brunvoll, J., Cyvin, S. J. and Schäfer, L. *J. Organometal. Chem. In press*; Cyvin, S. J., Brunvoll, J. and Schäfer, L. *J. Chem. Phys. In press*.
2. Cyvin, S. J., Cyvin, B. N., Brunvoll, J. and Schäfer, L. *Acta Chem. Scand.* **24** (1970) 3420.
3. Brunvoll, J., Cyvin, S. J. and Schäfer, L. *J. Organometal. Chem. In press*.
4. Hartley, D. and Ware, M. J. *J. Chem. Soc.* **1969** 138.
5. Fritz, H. P. *Habilitationschrift*, Universität München 1962.

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Investigation of Lactonic Acids in the Latex of *Euphorbium canariensis* L. Isolation of D-Glucaric Acid

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During the investigation of acids from succulent plants¹⁻³ it became evident that acids capable of forming lactones, often occur within this plant group. Evidence will here be advanced for the presence of D-glucaric acid in the latex of *Euphorbium canariensis* L. Aldaric acids have seldom been found in the free state in plants. However, D-glucaric acid has been found previously in the latex of *Ficus elastica* Roxb.⁴ and in *Phaseolus aureus* seedlings.⁵

Experimental. Latex of *Euphorbium canariensis* was repeatedly extracted with water (90°C). Calcium hydroxide solution was added to the eluates until pH 6.5 was obtained, followed by extraction with ether. On concentration of the aqueous solution a calcium salt precipitated (yield 4%). Titration of the calcium salt with perchloric acid: Found: $E=125.2$. (Calc. for $\text{C}_6\text{H}_8\text{O}_8\text{Ca}$: 124.11.) The salt was deionized with Dowex 50 (H^+) and furnished a syrup. Cryoscopic measurements gave a molecular weight of about 211. (Calc. for $\text{C}_6\text{H}_{10}\text{O}_8$: 210.14.) Back-titration after dissolution in sodium hydroxide at room temperature: Found: $E=104.5$. (Calc. for $\text{C}_6\text{H}_{10}\text{O}_8$: 105.07.) The acid was dried over phosphorus pentoxide at 0.02 mm Hg at 25°C overnight and gave a mixture, presumably consisting of D-glucaric acid, the two monolactones and the two dilactones.⁶ $[\alpha]_{\text{D}}^{20} = +93^\circ \rightarrow +45^\circ$ after 24 h ($c=1.5$; water). IR-spectrum identical with that of the authentic substance. The mixture was subsequently dried over phosphorus pentoxide at 0.01 mm Hg at 100°C until constant weight was obtained. (Found: C 41.41; H 3.60. Calc. for the dilactone $\text{C}_6\text{H}_8\text{O}_6$: C 41.39; H 3.45.) Dibenzylamide, m.p. 201–202°C, undepressed in mixture with an authentic sample. (Found: C 61.88; H 6.19; N 7.22. Calc. for $\text{C}_{20}\text{H}_{24}\text{O}_6\text{N}_2$: C 61.84; H 6.23; N 7.21.)

Paper chromatography. Paper chromatograms were run on Whatman No. 1 in the following solvent systems (v/v): A. Ethyl acetate, pyridine, water, 8:2:1. B. Ethyl acetate, acetic acid, formic acid, water, 18:3:1:4. C. Ethyl acetate, pyridine, acetic acid, water, 5:5:1:3. D. Ethyl methyl ketone, acetic acid, water, saturated with boric acid, 9:1:1.

Substances were located on chromatograms with the following reagents: a. Bromophenol Blue, 0.05%, in water. b. Hydroxylamine-ferrous chloride.⁷ c. Periodic acid-benzidine.⁸ d. Silver nitrate-sodium hydroxide.⁹ Chromatographic mobility of the acid in the solvent systems B and C was identical to that of the reference compound. The acid could be detected by either of the reagents quoted. The chromatographic mobility of the benzylamide in solvent system B was indistinguishable from that of the reference substance. The benzylamide was detected by reagent d.

Esterification with methanol and Dowex 50 (H^+). Esterification was effected by refluxing the acid (50 mg) with methanol and Dowex 50 (H^+) for 24 h. This treatment resulted in the conversion of the acid into its dimethyl ester and other reaction products, possibly the methyl ester monolactones and the dilactones (totally 56 mg). The chromatographic mobilities of the methyl esters and the dilactones