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BRIDGED FERROCENES—II[1]

CONFORMATIONAL PROPERTIES OF [m]FERROCENOPHANES*

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Abstract—The extent to which the molecular geometry and conformational freedom of the ferrocene nucleus is modified by interannular bridging has been investigated through a study of the spectral properties (particularly PMR) of a series of [m]ferrocenophane derivatives. In particular, the relative importance of cyclopentadienyl ring tilting, ring–ring torsion, and bridge mobility has been estimated for systems of differing bridge length.

INTRODUCTION

THE molecular structure of ferrocene has been thoroughly investigated by X-ray[2] and electron diffraction[3] techniques which have established that the molecule is centrosymmetric with the cyclopentadienyl rings disposed in parallel planes about the Fe atom. A large number of experimental observations has also accumulated to suggest that, in solution or in the vapour phase, the energy barrier to rotation of the rings is small.[4] From electron diffraction studies of ferrocene vapour, this barrier has been estimated[5] to be 0·9 kcal/mole which can be compared with the value of ca. 3·0 kcal/mole for rotation around the C—C bond in ethane.[6] It was further concluded[5] that the equilibrium conformation of the free ferrocene molecule is eclipsed although the staggered conformation is adopted in the crystal.[2]

When the cyclopentadienyl rings in ferrocene are linked by an interannular bridge, as in [m]ferrocenophanes (I),[7] two effects can be envisaged. It is obvious that the bridging group will impose a restriction upon the relative motion of these rings, the severity of which will be determined by the steric and conformational demands of the bridge. Further, if the bridging group cannot readily accommodate the inter-ring separation in the ferrocene nucleus, the cyclopentadienyl rings may be displaced from their preferred parallel plane arrangement. Some insight into the operation of these effects can be gained through a comparative study of the spectral properties of [m]ferrocenophanes (I) and their derivatives. Synthetic routes have now been developed for the preparation of a wide range of compounds of this type[1,8] and, in this paper, the conformational preferences of [2]-, [3]-, [4]-, and [5]ferrocenophanes (I; m = 2–5) will be discussed and compared.

Cyclopentadienyl ring tilting

Molecular models† suggest that the preferred inter-ring separation of ca. 3·3 Å in ferrocene[2,3] cannot be spanned by a chain of fewer than four C atoms unless the

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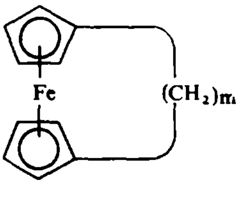
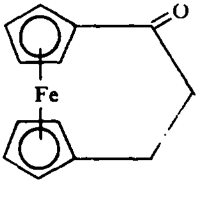
† Dreiding ferrocene stereomodels supplied by W. Büchi, Glasapparatefabrik, Flawil, Switzerland were used.

rings become mutually inclined. This conclusion has been substantiated by crystal structure determinations which have revealed that the dihedral angle between ring planes is ca. 9° in [3]ferrocenophan-1-one (II)[9] and ca. 23° in 1,1,2,2-tetramethyl-[2]ferrocenophane (III).[10]



I



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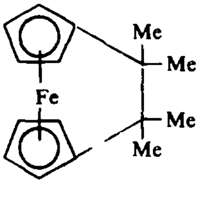

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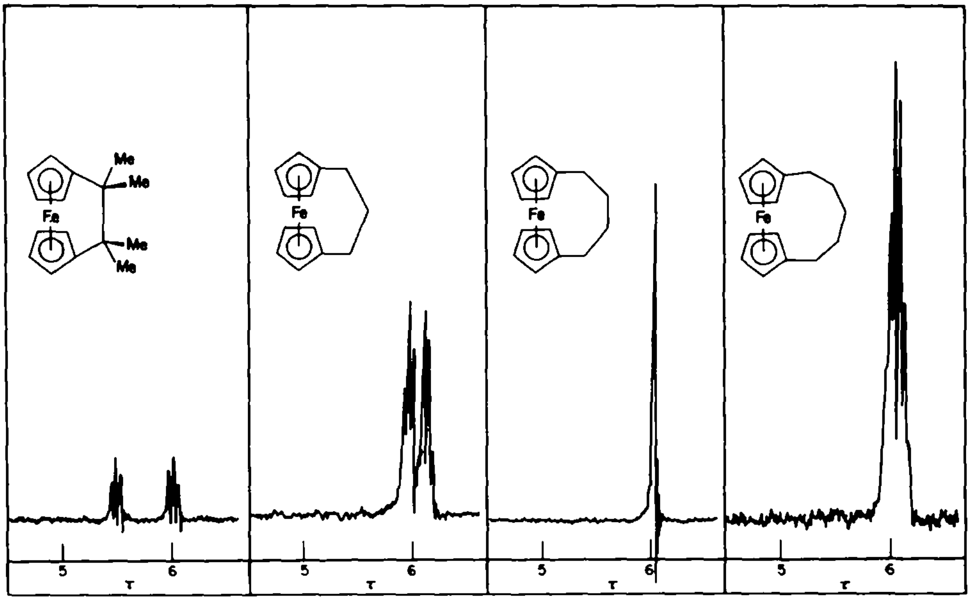
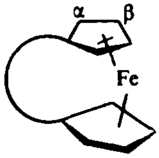


FIG. 1 Cyclopentadienyl proton patterns in the PMR spectra (C_6D_6 solutions) of [m]ferrocenophanes.

Perhaps the most striking manifestation of ring tilt in bridged ferrocenes is the variation in the cyclopentadienyl proton patterns in the PMR spectra of representative compounds of different bridge length. These are reproduced in Fig. 1. In general, alkyl substituents do not cause a noticeable difference in chemical shift between the α- and β-protons of the ring to which they are attached.[11] In the case of the highly splayed [2]ferrocenophane derivative (III), however, these protons appear as two unsymmetrical triplets separated (in C_6D_6) by 0·54 ppm, corresponding to an A_2B_2 spectrum where vicinal and cross-ring coupling constants are approximately equal and considerably smaller than the chemical shift difference between unlike protons.

This spectrum was discussed[12] by Rinehart *et al.* who suggested that the outcome of tilting the rings would be to bring the four protons α- to the bridge (see IV) closer to the Fe atom than the corresponding β-protons such that the former would experience the greater shielding influence. The PMR spectra of a number of other bridged and multibridged ferrocenes have been interpreted using similar arguments.[13, 14] Extending this hypothesis, the smaller splitting (in C_6D_6) of the ring proton resonance of [3]ferrocenophane (I; m = 3) implies a much reduced angle of ring tilt compared to the [2]homologue (III) and the singlet resonance of [4]ferrocenophane (I; m = 4) is in accord with an undistorted ferrocene nucleus.



IV

In the crystal, however, it has been established[9, 10, 15] that the Fe-ring C distances (and therefore, by inference, the Fe-ring H distances) are still approximately equal in ring-tilted ferrocenes. In other words, displacement of the rings from parallel planes occurs by a fulcrum action at the Fe atom which remains approximately equidistant from the five C atoms of each ring. For example, in the extreme case of the highly distorted ferrocenophane (III), the difference between the average Fe-C_α and Fe-C_β distances (see IV) is only 0·037 Å.[10] It is unlikely that these interatomic distances would vary significantly in solution from the values observed in the crystal and, in consequence, interpretation of the ring proton spectra (Fig. 1) on the basis of Fe–H proximity effects is open to question.

Using an MO approach to the bonding in metallocenes and related molecules, Ballhausen and Dahl have concluded[16] that considerable splaying of the rings (up to 45°) about the metal atom can occur in principle without significant loss in ring-metal bond strength. In such a situation, however, the altered molecular geometry requires hybridization of the metal d_{z^2}, d_{xy}, and $d_{x^2-y^2}$ orbitals, which are essentially nonbonding in ferrocene,[17] to produce three new mutually orthogonal orbitals oriented as shown in Fig. 2. This treatment has enjoyed spectacular success in accounting for

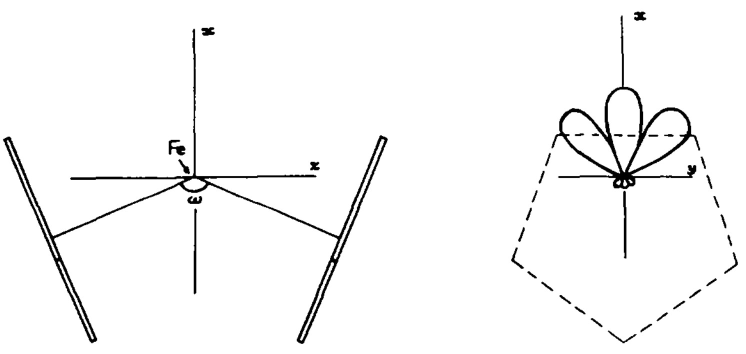


FIG. 2 Molecular orbitals for ring-tilted metallocenes (schematic) (see Ref. 16).

the existence, molecular geometry, and PMR spectral characteristics of a number of dicyclopentadienyl-transition metal hydrides and halides.[18]

In the case of a ring-tilted ferrocene, these hybrid orbitals would contain three non-bonding electron pairs leading therefore to an unsymmetrical distribution of electron density in the volume between the cyclopentadienyl rings (Fig. 2) and, in turn, a differential shielding of the protons attached to the α- and β-carbons. Further, the magnitude of this effect would increase with increasing ring tilt deformation, in accord with the experimental findings (Fig. 1). The question still remains unanswered as to which of the ring proton pairs (α- or β-) derives the greater shielding in such a situation.

The fine splitting of the ring proton resonance of [5]ferrocenophane (I; m = 5) is unlikely to be caused by a similar ring-tilt phenomenon since models show that the ferrocene nucleus can be readily spanned by a 5-carbon bridge without distortion of its preferred geometry. Conformational flexing of this bridge (*vide infra*), however, requires that the three central methylene groups (C_2–C_4) pass close to the four α-ring protons in turn. The chemical shift of these protons would thereby be influenced either by steric compression[19] or more probably by anisotropy effects associated with the CH_2—CH_2 bonds. Bridge inversion processes in [4]ferrocenophane and the lower homologues do not permit close interatomic approach of this nature.

The electronic spectra of ferrocene and its simple alkyl derivatives contain two weak bands ($\varepsilon < 100$) at 325 and 440 mμ which have been assigned[20] as symmetry forbidden electronic transitions of the N → Q type which derive intensity from vibrational distortion in the molecule. Although both bands contain much d-orbital character, some involvement of ring molecular orbitals in the "325 mμ" transition is indicated by the particular sensitivity of this absorption to substitution in the rings.[21] There is general agreement, however, that the "440 mμ" band represents a relatively pure (3d–3d) transition involving energy levels which are highly localized on the metal atom.[20–22] If non-bonding d-orbital hybridization accompanies ring-tilt deformation of the ferrocene nucleus, as suggested above, it would be expected that this would be reflected in the position and intensity of the "440 mμ" band.

The long wavelength absorption bands for a range of alkyl- and alkyl-bridged ferrocenes are listed in Table 1. The spectra of [4]- and [5]ferrocenophane (I; m = 4

TABLE 1. ELECTRONIC SPECTRA[a]

Compound	Absorption maxima mμ (ε) "325 mμ" band	"440 mμ" band
Ferrocene	326 (50)	440 (91)
1,1'-Dimethylferrocene	325 (60)	437 (102)
1,1'-Diisopropylferrocene	322 (91)	439 (101)
[5]Ferrocenophane (I; m = 5)	329 (76)	448 (110)
[4]Ferrocenophane (I; m = 4)	323 (71)	434 (100)
[3]Ferrocenophane (I; m = 3)	320 (84)	442 (184)
Tetramethyl[2]ferrocenophane (III)	326 (107)	466 (461)

[a] In absolute EtOH.

and 5 respectively) are closely similar to those of open-chain models e.g. 1,1'-dimethylferrocene. In the case of the ring-tilted ferrocene (III), however, the longest wavelength band has bathochromically shifted to 466 mμ with a marked (> fourfold) increase in intensity. A modest intensification of this absorption is also apparent for [3]ferrocenophane (I; m = 3) but little change in the "325 mμ" band was observed throughout the series examined. It appears unlikely that the changes observed in the position and intensity of the "440 mμ" band can be attributed solely to a lowered molecular symmetry since the "325 mμ" band should also be sensitive to symmetry factors. A more satisfactory explanation of the magnitude of the effect observed assumes changes in the relative energy levels of the iron non-bonding d-orbitals brought about by ring-tilt deformation.

Bridge mobility and ring–ring torsion

As discussed briefly in Part I of this series,[1] there is good evidence for conformational flexibility of the interannular bridges in [m]ferrocenophanes and their derivatives. Rapid inversion of the bridging groups is clearly demanded by the appearance of the methylene protons as sharp singlets* in the PMR spectra of representative members of the [3]-, [4]-, and [5]ferrocenophane classes. These are reproduced in Fig. 3.

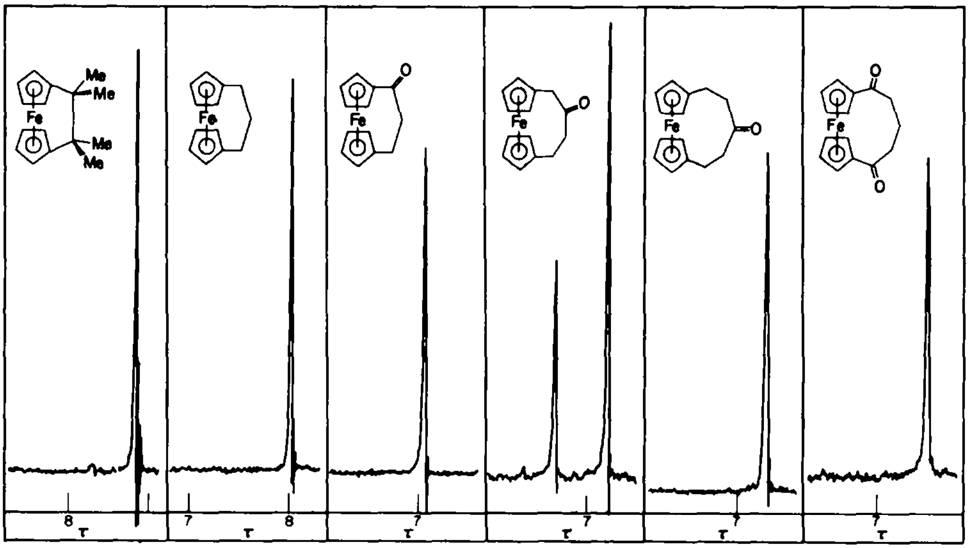


FIG. 3 Bridge proton resonances in the PMR spectra ($CDCl_3$ solutions) of [m]ferrocenophane derivatives.

In each case, facile conformational interconversion within the bridge effectively averages the magnetic environments of the protons associated with each methylene group producing equivalence on the PMR time scale.† In this connection, it may be noted that two enantiomorphous forms of the [2]ferrocenophane (III) are present

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* The methylene singlet in the spectrum of [3]ferrocenophane is only slightly broadened at −55°.

† Rosenblum *et al.* have argued[13] (on questionable grounds) that the rate of conformational equilibration of the bridge in [4]ferrocenophane is considerably diminished compared with that of the [3]homologue.

in the crystal and it has been pointed out[10] that there should be no great intrinsic barrier to their interconversion (e.g. in solution). The appearance of the four Me groups as a sharp singlet in the PMR spectrum of this compound (Fig. 3) supports this suggestion. The fortuitous coincidence in chemical shift between adjacent methylene groups in the bridges of these compounds is also noteworthy.

Bridge inversion processes in [m]ferrocenophanes permit relative oscillation of the cyclopentadienyl rings in the molecule. The extent to which this torsion can occur is controlled by the length of the bridge, becoming less restricted with increasing length. This effect can be seen in the variation in the ring proton patterns in the PMR spectra of [m]ferrocenophan-1-ones which are reproduced in Fig. 4.

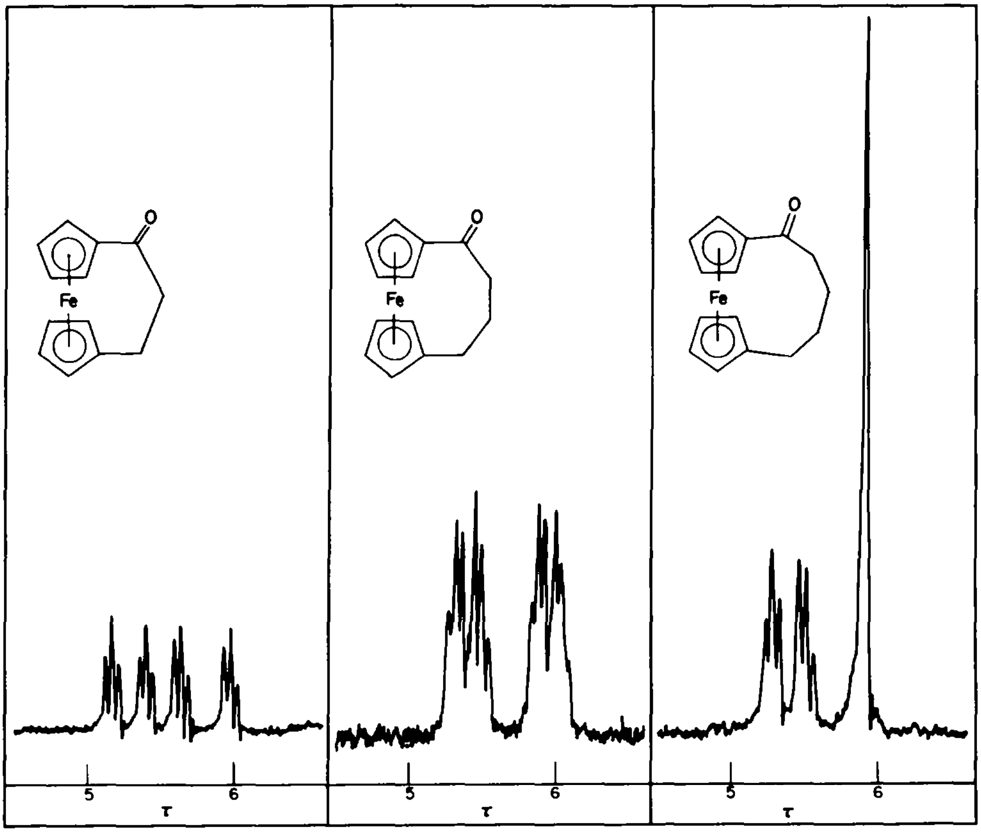

FIG. 4 Cyclopentadienyl proton patterns in the PMR spectra ($CDCl_3$ solutions) of [m]ferrocenophan-1-ones.

Rinehart[14] and Richards[23] *inter al.* have shown that the carbonyl group in acylferrocenes may exert a selective shielding influence on the various cyclopentadienyl protons depending upon the orientation which the carbonyl group is constrained to adopt relative to the ferrocenyl residue. With 1-acyl-1'-alkylferrocenes, where free relative rotation of the cyclopentadienyl rings is possible, the protons of the alkyl-substituted ring experience the same average magnetic environment and appear as a singlet in the PMR spectrum.[11] The singlet resonance observed (Fig. 4) for the analogous protons in the spectrum of [5]ferrocenophan-1-one, therefore, infers that a large measure of ring–ring torsion must still be possible despite the constraint imposed by the interannular bridge.

Predictably, this relative ring motion is severely reduced with the [3] homologue (II), in which case the two unique pairs of protons attached to the alkyl-substituted ring appear as well separated triplets, their average magnetic environments being different. Similarly, the splitting pattern observed for the ring protons of [4]ferrocenophan-1-one suggests that torsional motion of the rings is permitted only to a limited extent. Although the triplet appearing at lowest field in the spectra of all these bridged ketones can be confidently assigned to the pair of ring protons α- to the carbonyl group, unambiguous assignment of the remaining triplets is complicated in the case of [3]- and [4]ferrocenophan-1-one. On the basis of results obtained for a series of multibridged ferrocenophanones, the spectrum of the former has been interpreted[14] by Rinehart *et al.* However, spin decoupling experiments and examination of the spectra of suitably substituted derivatives (in progress) are required before full analysis of the spectra of these bridged ketones can be made with certainty.

CONCLUSIONS

An interannular bridge shorter than four carbons in length cannot be accommodated by the ferrocene nucleus without distortion of the preferred molecular geometry by ring tilting. The bridging chain in [m]ferrocenophanes (m = 2–5) undergoes rapid conformational exchange. The relative torsional freedom of the cyclopentadienyl rings in these compounds increases with increasing bridge length.

EXPERIMENTAL

With the exception of [5]ferrocenophan-3-one (m.p. 124·5–125·5°), which has been fully characterized and whose synthesis will be described in a forthcoming publication, all the compounds cited have been described previously in the literature.[1,8] PMR spectra were recorded in $CDCl_3$ or C_6D_6 solution as indicated on a Perkin–Elmer R10 spectrometer at 40 MHz using TMS as internal standard. Electronic spectra were obtained in absolute ethanol on a Unicam SP800A recording spectrometer.

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REFERENCES

[1] Part I: T. H. Barr and W. E. Watts, *Tetrahedron* **24**, 3219 (1968).
[2] J. D. Dunitz, L. E. Orgel and A. Rich, *Acta Cryst.* **9**, 373 (1956).
[3] E. A. Seibold and L. E. Sutton, *J. Chem. Phys.* **23**, 1967 (1955); R. K. Bohn and A. Haaland, *J. Organometal. Chem.* **5**, 470 (1966).
[4] E.g. see R. Riemschneider and W. Wucherpfennig, *Z. Naturforsch.* **21**^{b}, 929 (1966).
[5] A. Haaland and J.-E. Nilsson, *Chem. Comm.* 88 (1968).
[6] D. R. Lide, *J. Chem. Phys.* **29**, 1426 (1958).
[7] The nomenclature system proposed by B. H. Smith in *Bridged Aromatic Compounds*. Academic Press, New York (1964) has been adopted.
[8] For pertinent references see W. E. Watts, *Organometal. Chem. Revs.* **2**, 231 (1967).
[9] N. D. Jones, R. E. Marsh and J. H. Richards, *Acta Cryst.* **19**, 330 (1965).
[10] M. B. Laing and K. N. Trueblood, *Ibid.* **19**, 373 (1965).
[11] E.g. see R. A. Benkeser, Y. Nagai and J. Hooz, *Bull. Chem. Soc. Japan* **37**, 53 (1964).

[12] K. L. Rinehart, Jr., A. K. Frerichs, P. A. Kittle, L. F. Westmann, D. H. Gustafson, R. L. Pruett and J. E. McMahon, *J. Am. Chem. Soc.* **82**, 4111 (1960).

[13] M. Rosenblum, A. K. Banerjee, N. Danieli, R. W. Fish and V. Schlatter, *Ibid.* **85**, 316 (1963).

[14] K. L. Rinehart, Jr., D. E. Bublitz and D. H. Gustafson, *Ibid.* **85**, 970 (1963).

[15] I. C. Paul, *Chem. Comm.* 377 (1966); J. S. McKechnie, B. Bersted, I. C. Paul and W. E. Watts, *J. Organometal. Chem.* **8**, P29 (1967).

[16] C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.* **15**, 1333 (1961).

[17] For a discussion and leading Refs, see M. Rosenblum, *Chemistry of the Iron Group Metallocenes* Part I; p. 13 *et seq.* Interscience, New York (1965).

[18] Ref. 17, p. 48.

[19] Cf. S. Winstein, P. Carter, F. A. L. Anet and A. J. R. Bourn, *J. Am. Chem. Soc.*, **87**, 5247 (1965).

[20] D. R. Scott and R. S. Becker, *J. Chem. Phys.* **35**, 516 (1961); *Ibid.* **35**, 2246 (1961).

[21] Cf. K. I. Grandberg, S. P. Gubin and E. G. Perevalova, *Isvest. Akad. Nauk S.S.S.R., Ser. Khim.* 549 (1966); K. I. Grandberg and S. P. Gubin, *Ibid.* 551 (1966); H. Hennig and O. Gürtler, *J. Organometal. Chem.* **11**, 307 (1968).

[22] A. T. Armstrong, F. Smith, E. Elder and S. P. McGlynn, *J. Chem. Phys.* **46**, 4321 (1967).

[23] M. I. Levenberg and J. H. Richards, *J. Am. Chem. Soc.* **86**, 2634 (1964).