# Rotational Barriers and Dimer Association of Simple Polymethine Dyes

JOHANNES DALE, RAINER G. LICHTENTHALER and GERD TEIEN

Kjemisk Institutt, Universitetet i Oslo, Oslo 3, Norway

Bis(dimethylamino)tri-, penta-, and hepta-methinium dyes with various anions have been prepared, but give in no solvent a sufficient population of *cis* isomers for determination of rotational barriers in CC bonds by dynamic NMR spectroscopy. Rotational barriers in CN bonds have been redetermined, and reasons for conflicting results in the literature are given. Vapour pressure osmometry shows that these dyes are dissociated in water and methanol, partially dissociated in acetone, and ion pairs in 1,2-dichloroethane. In chloroform the penta-methinium perchlorate is a monomeric ion pair at high dilution but dimeric in moderately concentrated solution; with other anions mixtures are present.
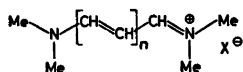
1, n = 0, "monomethine"
2, n = 1, "trimethine"
3, n = 2, "pentamethine"
4, n = 3, "heptamethine"

Cyanine dyes, the simplest representatives of which are tetramethylformamidinium salts (*1*) and their vinylogues, the dimethylaminopoly-enylidene dimethylammonium salts (*2 − 4*), have attracted much interest from physical and theoretical chemists because they are simple examples of stable open-chain compounds whose structure is represented by resonance between two equivalent mesomeric structures. The resulting one-and-a-half bond character is expected to make rotation about the CC and CN bonds more hindered than in single bonds and less hindered than in double bonds. *Cis-trans* isomerism would therefore be possible although individual isomers might not be separable at room temperature.

All available data [1-6] indicate that the largely favoured isomer of polymethine dyes in solution is all-*trans*, and this is also found in reported crystal structures.[6-14] Nevertheless, solutions of a more complex cyanine of benzothiazolium type, with a chromophore length corresponding to a "nonamethine", were found by Zechmeister and Pinckard [15] to contain three isomers in thermodynamic equilibrium, recognizable as distinct zones on a chromatographic column, each eluted zone giving the same spectrum and the same isomer mixture on repeated chromatography. Thus, the life-time at room temperature exceeds the time between desorption and new adsorption during migration on the column, but is shorter than the time required for manipulation of solutions.

As to the exact magnitude of the rotational barriers in the bonds of the unsaturated chromophoric system, hence their double-bond character, the available data are contradictory and confusing. Theoretical calculations [6,16,17] predict rather similar bond orders (60 − 70 % π bond character) and only a slight weakening of the CN bond with increasing chain length in the homologous series *1 − 4*. Rotational barriers are therefore expected to be higher than in amides [18] (~85 kJ mol⁻¹).

Experimentally, information about the bond order in the CN bonds can be obtained by dynamic NMR spectroscopy from the pairwise exchange of *N*-methyl sites in the simple cyanines [4,19] even when only the all-*trans* isomer is populated. Published barriers [4] from the early days of dynamic NMR for the dyes *2 − 4* were given as Arrhenius energies. These are obviously too low but the data do not permit

recalculation of the only reliable parameter, [18],[20] the free-energy of activation at the coalescence temperature. It was therefore necessary to redetermine these barriers.

Information about the bond order in the CC bonds can be obtained by dynamic NMR spectroscopy only if *cis* isomers are substantially populated in the thermodynamic equilibrium. Since this is not the case for the simple cyanines studied so far, the only possibility has been to populate unstable mono-*cis* isomers photochemically and study their rates of reconversion to the all-*trans* isomer. This was first done on the related dipyrrolidylpentamethinium perchlorate at low temperature using conventional kinetics,[1] and later by flash photolysis techniques at higher temperature.[5] The former method led to an unacceptably low Arrhenius energy (24 kJ mol⁻¹), but the latter method gave more reasonable values of about 63 kJ mol⁻¹, although again values of only 25 kJ mol⁻¹ were reported for flash photolysis at low temperatures.

Our approach has been to seek chemical and physical conditions which would favour *cis* isomers in the equilibrium with the all-*trans* isomer to such an extent that these become observable by NMR spectroscopy, thus allowing a determination of the barrier for their mutual interconversion. Since the formal cationic charge of these molecules resides mainly on the nitrogen atoms at each end, one way would be to prepare dyes with anions more nucleophilic than the most widely used perchlorate anion. These might show a tendency to form ion pairs instead of dissociated ions in appropriate solvents. With sufficient chain length, a bent mono-*cis* isomer might then, in a chelating manner, allow both nitrogen atoms to come closer to the same anion than is possible for the extended all-*trans* isomer.

Sterically unhindered *cis* isomers cannot exist for the shortest chain, the "trimethine" (*2*). On the other hand, the chemical stability decreases with chain length. Attention was therefore focused on the "pentamethine" and
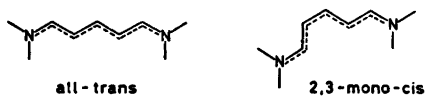

Fig. 1. Possible planar isomers of the bis (dimethylamino) pentamethinium cation.
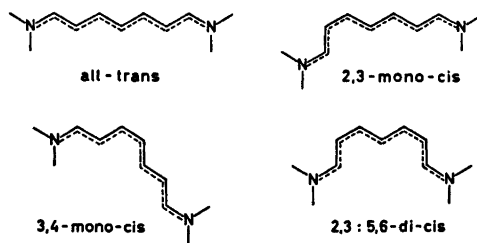

Fig. 2. Possible planar isomers of the bis (dimethylamino) heptamethinium cation.

"heptamethine" dyes (*3* and *4*). The NN distance in the only sterically unhindered *cis* isomer of the pentamethine (2,3-mono-*cis*) is however only 12 % shorter than in the all-*trans* isomer (Fig. 1). For the heptamethine the shortening of the NN distances in some of the sterically unhindered isomers is more marked; thus for 2,3-mono-*cis*, 3,4-mono-*cis*, and 2,3:5,6-di-*cis* it is about 10, 15 and 25 % respectively (Fig. 2). This may be the reason why the presence of small amounts of *cis* isomers in the equilibrium, especially at higher temperatures, is indicated in the UV-spectrum of dipiperidylheptamethinium perchlorate [6] but much less in the corresponding pentamethine.*

We now report that a series of such polymethines, irrespective of the identity of the anion, failed to favour *cis* isomers in solvents that would be expected to promote ion pairing, but gave instead dimeric ion pairs with preservation of the extended all-*trans* configuration. No information was therefore obtainable about the rotational barriers in the CC bonds. New $\Delta G^{\neq}$ values were obtained for the rotational barriers in the CN-bonds and together with recalculated values from published kinetic data, these are satisfactorily coherent and all above 63 kJ mol⁻¹.

PREPARATION OF CYANINE DYES WITH VARIOUS ANIONS

The bis (dimethylamino) trimethinium dyes (*2*) could be easily prepared from 1,3,3-trimethoxypropene, dimethylamine and the dimethylammonium salt having the desired

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* The reported assignment [16] of various crystalline forms of bis (dimethylamino) pentamethinium perchlorate to all possible *cis* isomers does not seem to have ever been documented.

Table 1. Data for bis (dimethylamino)polymethinium salts.

| | M.p/°C | Mol. weight by v.p. osmometry [a] | | | | M.W. calc. |
		$CHCl_3$	$(CH_2Cl)_2$	$(CH_3)_2CO$	CH_3OH	
Trimethinium (2)						
perchlorate	120	227		113	113	226
chloride	197 [b]	80 [c]			66 [c]	163
bromide	212	175 [c]			97 [c]	207
iodide	189	252			128	254
Pentamethinium (3)						
perchlorate	169	252	252	163	127	252
chloride	185	154 [c]			94	188
bromide	205	233			117	233
iodide	192	277			140	280
hexafluorophosphate	198	307				298
hexafluoroantimonate	221	381				389
thiocyanate	130	212				211
tosylate	135	327				324
picrate	173	381				381
Heptamethinium (4)						
perchlorate	178	281	286	174	142	278
chloride	148	220			(215)	214
bromide	152	255			129	259
iodide	182	303			153	306
thiocyanate	147	233				237
acetate	145	235				238

[a] At 37 °C except for methanol (45 °C). [b] Crystallized as monohydrate melting first around 70 °C. [c] Hygroscopic.

anion. Preparative procedures [21,22] for the corresponding pentamethinium and heptamethinium dyes (*3* and *4*) involve isolation in the form of perchlorates, and attempts to modify the procedures to obtain directly the desired salts failed. Anion exchange was therefore used, taking advantage of the insolubility of potassium perchlorate in ethanol, but the method is obviously limited to those anions whose potassium salts are soluble in ethanol. The compounds obtained are shown in Table 1.

The trimethine and pentamethine dyes are stable compounds and can be chromatographed on various adsorbents from methylene chloride or ethylene chloride. No separation into different zones could be detected, so that under these conditions only the all-*trans* isomer seems to be present.

The heptamethine dyes are much more sensitive and decompose when chromatographed, especially on alumina. The best system was calcium phosphate using 1,2-dichloroethane as eluent. The thiocyanate was most suitable for solubility reasons. After a first chromatographic separation of yellow impurities, the main red zone was rechromatographed and produced a very weak additional red zone. On elution, its IR spectrum was identical with that of the main zone. The amount of this second isomer was, however, too small to be detected by NMR spectroscopy of the initial or eluted solutions.

DISSOCIATION AND DIMERIZATION STUDIES BY VAPOUR-PRESSURE OSMOMETRY

Since the conditions for enforcement of *cis* isomers were believed to be those favouring ion pairing, it became necessary to determine the apparent molecular weight of the cyanines in various solvents. This was done most easily by vapour pressure osmometry,[23] which can also reveal dissociation-association equilibria [24] as deviations from linearity in a plot of measured specific resistance value against concentration. Both penta- and heptamethinium perchlorate gave in methanol straight lines which extrapolated at infinite dilution to half the molecular weight, showing that full dissociation occurs. The same compounds in ethylene chloride gave also straight lines, but these extrapolated to the correct molecular weight, so that here simple ion pairs are present. Acetone

showed an intermediate behaviour, since the curves were not straight and extrapolated to intermediate values (63 % of the correct molecular weight) indicating coexistence of ions and ion pairs even at high dilution.

A most surprising result was obtained using chloroform as solvent. At low concentrations the curve for pentamethinium perchlorate extrapolated to the molecular weight of a monomeric ion pair, but bent off at concentrations above 0.07 M and extrapolated in this region to the molecular weight of a dimeric ion pair. Similar but less bent curves were obtained for all the other anions. In Fig. 3 these curves have been transformed to a common molar scale, and it is clear that in the concentration range used there is coexistence of monomeric and dimeric species, possibly also higher species. When the cation is more complex and lipophilic, as in a cyanine of benzothiazolium type with a chromophore length corresponding to a "heptamethine" (Fig. 3), the curve suggests higher species; thus, extrapolation from the highest concentration gives at least a hexameric ion pair.

Aggregation and, more specifically, dimer formation has been observed earlier by UV spectroscopy [25-29] for the more complex cyanine dyes with larger lipophilic cations, but then usually only in water solution or in alcoholic solvents at low temperature under conditions of high viscosity. This may be the first observation of aggregation in lipophilic solvents at room temperature and of aggregation studied by direct molecular weight determination.

It is of interest that dimerization of simple pentamethines is most pronounced when the anion is least nucleophilic (i.e. perchlorate). This supports earlier observations on more complex cyanines that aggregation occurs by stacking of cations [7,8,25] leaving the anions between the stacks; further, that the perchlorate gives dimer more easily than the iodide,[26] and that the all-trans isomer is preferentially dimerized.[29]

Chloroform solutions of the pentamethinium perchlorate having concentrations between 70 and 250 g/l (0.28 and 1.0 M) show just below the boiling point a remarkable separation into two phases. The lower phase is more dilute (0.28 M), the upper more concentrated (1.0 M) The concentration of dye in each of the two phases is independent of the initial concentra-
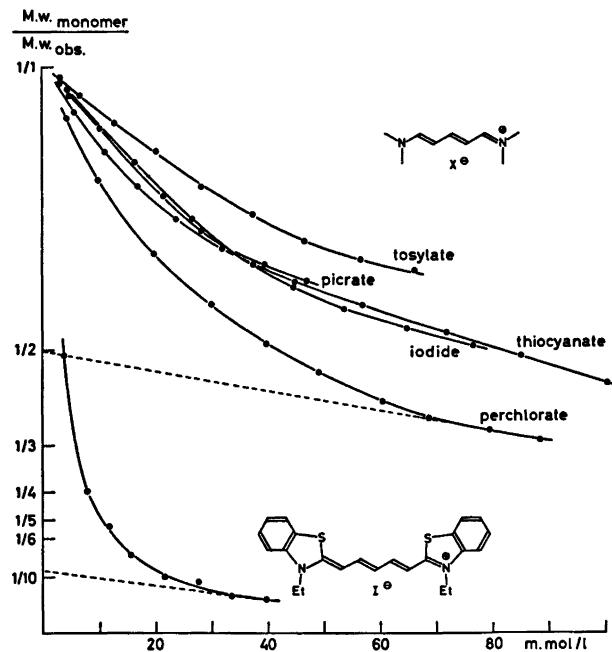

Fig. 3. Vapour-pressure osmometric curves for bis(dimethylamino)-pentamethinium salts in chloroform.

tion, but of course the relative volumes must vary. Thus, separation into two phases of equal volume takes place only at a concentration of 160 g/l (0.64 M). The concentration of the more dilute lower phase is well above the limit (0.07 M) for which molecular weight determinations indicate dimeric ion pairs, and it is tempting to suggest that the upper phase may contain high-molecular stacked aggregates requiring less chloroform for solvation.

The NMR spectra are identical in all concentration ranges, including the very dilute solutions for which molecular weight determinations indicate monomeric ion pairs.

Dimerization of ion pairs was not observed for the trimethinium or heptamethinium dyes. The trimethinium cation is probably too small so that the repulsive charge forces dominate, and the heptamethinium salts may not be sufficiently soluble to reach the necessary concentration.

ROTATIONAL BARRIERS IN THE CN BONDS

The tri-, penta- and heptamethines (2 – 4) all show the same type of NMR spectrum irrespective of anion and solvent. The vicinal coupling constants for the methine protons are all about 12 Hz as reported earlier [2-4,6] for this type of cyanine dyes, indicative of an all-trans isomer (cyclic polymethines with enforced cis structure [30] show vicinal coupling constants of about 8 Hz). Temperature variation produced only a change in the methyl region from a single line in the fast-exchange spectrum to two equal-intensity lines in the slow-exchange spectrum, the coalescence temperatures being at ~160, ~80, and ~30 °C for the tri-, penta-, and heptamethines, respectively (Table 2). No minor lines were detected in any part of the spectra, not even at temperatures of −60, −95 and −120 °C, using $CDCl_3$, CD_3OD or $CHFCl_2$ as solvent. Thus, the process corresponds to rotation about the CN bond in a single all-trans isomer.

The barrier heights have been calculated as activation free energies ($\Delta G^{\neq}$) at the coalescence temperature (Table 2) and are seen to be much higher than the Arrhenius energies (E_a) reported by Scheibe [4] for the same perchlorates, but agree with the reported observation [3] that the trimethinium perchlorate shows two methyl

signals up to 110 °C. The disagreement arises because E_a values can only be obtained from an Arrhenius plot involving kinetic parameters collected also outside the reliable temperature range of the NMR method.

For a given polymethinium cation the height of the rotational barrier is surprisingly constant and independent of the nature of the anion, in spite of the observed differences in degree of dissociation of the ion pair and the degree of association of the cation. Only a slight influence of the solvent is noticeable; in comparison with acetonitrile, 1,1,2,2-tetrachloroethane tends to give slightly higher barriers, whereas chloroform and methanol tend to give slightly lower barriers. The latter solvents may interact by hydrogen bonding to one nitrogen lone pair to favour one of the resonance structures. This is in agreement with the further observation that addition of small amounts (3 – 12 %) of trifluoroacetic acid lowers the barrier quite considerably; thus T_c for the pentamethinium cation changes from 90 to −10 °C.

The $\Delta G^{\neq}$-barriers are seen to decrease surprisingly rapidly with chain length. Theoretical calculations for the isolated symmetric cation predict that the double-bond character should decrease only slowly with chain length within the range of 70 – 60 %. There is, however, no need to expect a direct correlation between double-bond character in the ground state and height of the rotational barrier, although this is often observed. The actual magnitude of these barriers is also surprisingly low, since the amide group with double-bond character of only 40 % has a rotational barrier as high as ~85 kJ mol⁻¹.[18] It seems likely that during rotation of a given CN bond the electronic system readjusts continuously so as to favour the mesomeric structure having a single bond at that point. This electron displacement may become easier the longer the chromophore.

That the barrier for the monomethine is then not the highest of all,[19] is readily understood on the basis of steric hindrance to planarity from methyl group interaction, which will raise the energy of the resting molecule but not the transition state for internal rotation. This situation is also reflected in the relative difficulty of its preparation,[21] its anomalously low UV-extinction,[21] and the small chemical-shift difference for its methyl groups (Table 2).

Table 2. CN rotational barriers in bis (dimethylamino)polymethinium salts.

Salt	Solvent	$\Delta\nu$/Hz at 100 MHz	T_c/K	$\Delta G^{\ddagger}$/kJ mol^{-1}	E_a/kJ mol^{-1} Lit. value
Monomethinium (*1*)					
perchlorate	CDCl$_3$	6 [a]	293	65.5 [b]	73.5 [19]
Trimethinium (*2*)					
perchlorate	Ph$_2$CO	16	428	93.5	71.5 [4]
bromide	Ph$_2$CO	16	428	93.5	
iodide	Ph$_2$CO	16	428	93.5	
Pentamethinium (*3*)					
perchlorate	CHCl$_2$CHCl$_2$	21	363	78.0	42.0 [4]
perchlorate	CD$_3$CN	19	353	76.0	
hexafluorophosphate	CHCl$_2$CHCl$_2$	21.5	364	78.0	
hexafluoroantimonate	CD$_3$CN	19	351	76.0	
bromide	CD$_3$CN	18	353	76.5	
tosylate	CD$_3$CN	19	353	76.0	
picrate	CD$_3$CN	19	353	76.0	
Heptamethinium (*4*)					
perchlorate	CHCl$_2$CHCl$_2$	20	315	67.5	29.5 [4]
perchlorate	CD$_3$CN	19	303	65.0	
perchlorate	CD$_3$OD	19	293	63.0	
bromide	CDCl$_3$	28.5	303	64.0	
bromide	CD$_3$OD	19	293	63.0	
iodide	CHCl$_2$CHCl$_2$	22	316	67.5	
iodide	CD$_3$CN	19	303	65.0	
acetate	CDCl$_3$	26	297	62.5	
acetate	CD$_3$OD	18.5	295	63.0	

[a] At 60 MHz. [b] Recalculated from ref. 19.

A NOTE ON ROTATIONAL BARRIERS IN THE CC BONDS

The same order of magnitude is expected for the rotational barriers of the CC bond as for the CN bond. Only pentamethines have been examined, the one resembling most closely our bis-dimethylamino derivative being the dipyrrolidyl derivative (as perchlorate). The flash-photolytic data [5] in ethanol in the temperature range 255–314 K give a barrier height expressed in Arrhenius energy E_a of 65 kJ mol^{-1}. If the kinetic data (as read off from the published curves) are expressed less ambitiously as Eyring free energies of activation at each temperature, roughly the same value of $\Delta G^{\ddagger}$ ∼70 kJ mol^{-1} is obtained over this whole range, implying that the activation entropy is very small, as it should be in a unimolecular reaction. However, for the temperature range 215–252 K a very low barrier of $E_a = 25$ kJ mol^{-1} has been given,[5] but if again the kinetic data are expressed as $\Delta G^{\ddagger}$ values, barriers of 65–70 kJ mol^{-1}, increasing with temperature, are obtained. These data would imply that $\Delta H^{\ddagger}$ is only about 20 kJ mol^{-1} and $\Delta S^{\ddagger}$ − 200 J mol^{-1} K^{-1}, a very unlikely enthalpy barrier for a bond with double-bond character, and an unacceptably high activation entropy for a unimolecular reaction. The earliest data obtained by conventional kinetics [1] at 103–223 K are similar ($E_a = 24$ kJ mol^{-1}); from the reported half-times $\Delta G^{\ddagger}$ values of 60–65 kJ mol^{-1} can be estimated. Clearly the low-temperature data must be inaccurate, and a $\Delta G^{\ddagger}$ barrier of 70 kJ mol^{-1} should be accepted for the process 2,3-mono-*cis* → all-*trans* in the pentamethine. For the reverse reaction $\Delta G^{\ddagger}$ then becomes 75 kJ mol^{-1}, since the 2,3-mono-*cis* isomer is ∼5 kJ mol^{-1} higher in energy (1,2-mono-*cis* is still higher).[6]

Thus, the rotational barriers in CC and CN bonds agree very closely in this pentamethine, which seems reasonable since the theoretical values for double-bond character are similar, and any displacement of the electronic system to favour one mesomeric structure during internal rotation should reduce all barriers to a similar extent.

EXPERIMENTAL

Preparation of polymethine dyes. The 3-dimethylaminopropenylidene dimethylammonium halides (*2*) were prepared by refluxing a solution of equimolar quantities of 1,3,3-trimethoxypropene, dimethylamine and dimethylammonium halide in ethanol for 24 h. After evaporation to dryness, the residue was redissolved in a little ethanol and crystallized at 0 °C. Samples of the corresponding perchlorate were received as gifts from Professors B. W. Matthews, University of Oregon, and F. Dörr, Technische Universität München.

The 5-dimethylaminopenta-2,4-dienylidene dimethylammonium salts (*3*) and the 7-dimethylaminohepta-2,4,6-trienylidene dimethylammonium salts (*4*) were synthesized and isolated as perchlorates by known methods.[21,22] Exhange of anion was carried out by adding an equimolar amount of the potassium salt of the desired anion dissolved in the smallest possible volume of ethanol to a solution of the polymethinium perchlorate in ethanol. After concentration of the solution to half its volume, potassium perchlorate precipitated and was filtered off. Further concentration precipitated the polymethinium salt which was then recrystallized from ethanol or 1,2-dichloroethane/light petroleum. Melting points and molecular weights are given in Table 1.

Chromatography. The adsorbents used were Al_2O_3 (Woelm, neutral), silica (Merck Kieselgel 60), $CaCO_3$ (Merck), $ZnCO_3$ (Merck) and $Ca_3(PO_4)_2$. The eluents were either 1,2-dichloroethane or dichloromethane containing 2 % of methanol.

Molecular weight determinations. A Knauer vapour-pressure osmometer (Knauer Dampfdruck-osmometer) was used generally at a temperature of 37 °C (for methanol at 45 °C) and equilibration times were between 3 and 8 min. The results were plotted as measured calibrated "specific resistance value" ($\Delta R/C$) against concentration and the curves extrapolated to zero concentration. The curves displayed in Fig. 3 were obtained by dividing each observed $\Delta R/C$ value with the extrapolated value and the concentration values with the (monomeric) molecular weight.

NMR measurements. ¹H NMR spectra at 100 MHz were recorded on a Varian HA 100 15D instrument. Solvents for low-temperature spectra were $CDCl_3$, CD_3OD or $CHFCl_2$, for high-temperature spectra CD_3CN, $CDCl_3$, $ClCH_2CH_2Cl$, CD_3OD or benzophenone. Rate constants at coalescence were estimated from the simple relation $k = (\pi/\sqrt{2})\Delta\nu$ and expressed according to Eyring as $\Delta G^{\neq}$.

REFERENCES

1. Baumgärtner, F., Günther, E. and Scheibe, G. *Z. Electrochem. Ber. Bunsenges. Phys. Chem. 60* (1956) 570.
2. Scheibe, G., Seiffert, W., Wengenmayr, H. and Jutz, C. *Ber. Bunsenges. Phys. Chem. 67* (1963) 560.
3. Dähne, S. and Ranft, J. *Z. Phys. Chem. Leipzig 224* (1963) 65.
4. Scheibe, G., Jutz, C., Seiffert, W. and Grosse, D. *Angew. Chem. 76* (1964) 270.
5. Dörr, F., Kotschy, J. and Kausen, H. *Ber. Bunsenges. Phys. Chem. 69* (1965) 11.
6. Scheibe, G., Heiss, J. and Feldmann, K. *Ber. Bunsenges. Phys. Chem. 70* (1966) 52.
7. Hoppe, W. and Baumgärtner, F. *Z. Kristallogr. 108* (1957) 328.
8. Wheatley, P. J. *J. Chem. Soc.* (1959) 3245, 4096.
9. Smith, D. L. and Luss, H. R. *Acta Crystallogr. B 28* (1972) 2793.
10. Matthews, B. W., Stenkamp, R. E. and Colman, P. M. *Acta Crystallogr. B 29* (1973) 449.
11. Sieber, K., Kutschabsky, L. and Kulpe, S. *Krist. Techn. 9* (1974) 1101, 1111.
12. Zedler, A. and Kulpe, S. *J. Prakt. Chem. 317* (1975) 38.
13. Ziemer, B. and Kulpe, S. *J. Prakt. Chem. 317* (1975) 185, 199.
14. Selzer, J. O. and Matthews, B. W. *J. Phys. Chem. 80* (1976) 631.
15. Zechmeister, L. and Pinckard, J. H. *Experientia 9* (1953) 16.
16. Leupold, D. *Z. Phys. Chem. Leipzig 223* (1963) 405.
17. Radeglia, R., Gey, E., Nolte, K. D. and Dähne, S. *J. Prakt. Chem. 312* (1970) 877.
18. Kessler, H. *Angew. Chem. 82* (1970) 237.
19. Ranft, J. and Dähne, S. *Helv. Chim. Acta 47* (1964) 1160.
20. Anet, F.A.L. and Anet, R. *Det. Org. Struct. Phys. Methods 3* (1971) 344.
21. Malhotra, S. S. and Whiting, M. C. *J. Chem. Soc.* (1960) 3812.
22. Nikolajewski, H. E., Dähne, S. and Hirsch, B. *Chem. Ber. 100* (1967) 2616.
23. Chylewski, C. and Simon, W. *Helv. Chim. Acta 47* (1964) 515.
24. Elias, H. G. and Lys, H. *Makromol. Chem. 92* (1966) 1.
25. Zimmermann, H. and Scheibe, G. *Z. Electrochem. Ber. Bunsenges. Phys. Chem. 60* (1956) 566.
26. Levinson, G. S., Simpson, W. T. and Curtis, W. *J. Am. Chem. Soc. 79* (1957) 4314.
27. West, W. and Pearce, S. *J. Phys. Chem. 69* (1965) 1894.
28. Scheibe, G. and Worz, O. *Angew. Chem. 78* (1966) 304.
29. Pearce, S. and Grum, F. *J. Phys. Chem. 71* (1967) 1316.
30. Scheibe, G., Heiss, J. and Feldmann, K. *Angew. Chem. 77* (1965) 545.