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Monthly
Ecumenical
Letters from
Laboratories
Of
N - M - R
No. 18

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MELLON INSTITUTE

4400 FIFTH AVENUE
PITTSBURGH 13, PA.

March 7, 1960

Dr. Aksel A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.


Dear Aksel:

The plug attached above has been found to be very handy as a temporary stopper for 5 mm. O.D. sample tubes. It is made of polyethylene and can be obtained at \$6.00 per thousand (in any quantity) from

Caplugs Division
Protective Closures Co., Inc.
2207 Elmwood Avenue
Buffalo 23, New York

This particular plug is No. K-3. The company makes similar plugs and caps in many sizes and shapes.

Yours truly,



PCLauterbur:pok

Fellow

Department of Chemistry,
Imperial College,
Imperial Institute Road,
LONDON S.W.7

Drs. AA. Bothner-By & B.L. Shapiro:

18th March, 1960.

Gentlemen:

Proton resonance spectra are often helpful in studying the transition metal hydrides, most of which seem to have a sharp proton resonance line in a region about 7-20 p.p.m. on the high field side of silicon tetramethyl. In particular, a sharp line in this region shows the presence of these hydrides in aqueous solutions where they are not easily detected by other methods.

However, since the resonances of protons bonded to some atoms (e.g. in HI) which are not transition metals also occur at fairly high fields, we are investigating certain other hydrides of non-transition elements. An example is the hydrides of tetravalent tin. In the n-butyl hydrides the proton resonances are centred on the low field side of silicon tetramethyl, their position depending on the number of alkyl groups bonded to the tin atom. So a proton is not always greatly diamagnetically shielded when bonded to a heavy atom; it may be significant that the tin d-orbitals are filled and not greatly involved in bonding to other groups in the hydride molecules.


The values of the shifts suggest that there may be two opposing effects modifying the hydride shift position. To explain a similar phenomenon in the P^{19} resonances of alkyl silicon fluorides [Schnell and Rochow, J.A.C.S., 78, 4178 (1956)] it was suggested that an inductive effect was opposed by the effects of Si-F d π -p π bonding. This type of interaction is unlikely in hydrides, and another possibility is that steric interactions do not allow the molecules to have a regular tetrahedral configuration at the tin atom, and that this alters the contributions from anisotropic induced moments in the Sn-C bonds.

Compound	τ	$J_{H-Sn_{117}}$	$J_{H-Sn_{119}}$	J_{119}/J_{117}
SnH ₄	6.11	1842 o.p.s.	1933 o.p.s.	1.049
(n-But) ₂ SnH ₂	5.23	2219	2119	1.047
(n-But) ₃ SnH	7.93	1650	1722	1.044

Those molecules containing the isotopes Sn¹¹⁷ (I = $\frac{1}{2}$, $\mu = -0.9949$, abundance 7.67%) and Sn¹¹⁹ (I = $\frac{1}{2}$, $\mu = -1.0409$, abundance 8.68%) give rise to pairs of satellite lines with splittings of about 2000 o.p.s. The ratios of the splittings are constant and, as expected, are equal (within the limits of error) to the ratio of the magnetic moments of the tin isotopes. The splittings are somewhat larger than those observed for protons bonded to lighter atoms whose nuclei have magnetic moments of about the same magnitude as those of tin. Possibly the contributions to such splitting from the electron dipole and electron orbital interactions are relatively more important in the tin hydrides.

As with the shifts, the value of the splitting of the dihydrides does not lie between those of the other two. Pople (Pople, Schneider and Bernstein, p. 195) has derived a relation between the orbital contributions to the splitting and the shielding anisotropies, which we hope may be applicable to molecules of this type. Apart from the comparison with transition metal hydrides, the resonances of protons bonded to heavy atoms are of interest since they may provide information about interactions which are of minor importance in lighter molecules.

Yours sincerely,



P. E. Potter
L. Pratt.

NMR STUDY OF THE ISOMERIC PINOCAMPHONES

Use has been made of the formula $\Delta\sigma = \frac{\Delta\chi(1 - 3\cos^2\theta)}{3R^3}$ developed

by McConnell (1) for the prediction of the direction and approximate magnitude of hydrogen resonance shifts caused by magnetic fields from induced currents in groups of neighbouring electrons. Recently we have been examining some olefins and ketones in the pinane (I) (Figure 2) series and we find that their spectra can be explained qualitatively with the aid of this formula.

There have been some recent speculations on the stereochemistry of the pinocamphones (2) and it has been suggested that the normal and iso compounds have the conformations given by (II) and (III) respectively. Earlier workers have proposed II and IV as probable conformations (3).

Calculations of $\Delta\sigma$ for the methyl groups 8, 9 and 10 from the above expression indicates that a ready distinction should be possible between the "up" and "down" ring conformations (III) and (IV) respectively. Figure 1 shows the dependence of $\Delta\sigma$ (in terms of $10^{-2}\Delta\chi$) on the degree of planarity of the ring.

First consider the "up" conformation (III). Here the 9-methyl should be strongly shielded compared with that of pinane and the resonance must therefore occur at high field strengths; the 8-methyl should be relatively slightly shielded and the resonance should therefore only show a small shift to high field. By comparison, the 9-methyl in the "down" conformation of the cyclohexane ring (II) and (IV) should be only slightly shielded and the 8-methyl slightly deshielded.

It can be seen from the spectra that the well separated 8 and 9-methyl group resonances in the two ketones occur at almost identical frequencies. Using cis-pinane as a reference compound, the 9-methyl shows a shift to high field of about 0.15 ppm (6 cps) and the 8-methyl a shift to low field of nearly the same amount. The great similarity of the two spectra (Figure 2) with respect to these two methyl groups suggests that the ring conformations are the same and the relative magnitudes of these shifts indicate that the "down" conformation is to be preferred.

The above expression also predicts that the 10-methyl group is deshielded in an equatorial configuration but not significantly shielded in an axial configuration by the induced moment of the C = O electrons.

The doublet characterising the 10-methyl group occurs at a higher field for isopinocampnone than for pinocampnone (Figure 2). This was confirmed by the spectra of their benzene solutions when the doublets were well separated from the 8 and 9-methyl resonances. A comparison of the spectra of cis-pinane and isopinocampnone reveals that the doublets of the 10-methyl groups occur at virtually the same frequencies. The corresponding doublet of pinocampnone occurs at 0.125 ppm (5 cps) to low field.

A comparison of these results with the predictions set out above, would favour the conformations given in (II) and (IV) respectively.

The differences in ppm between the 10-methyl resonances of structures (II) and (IV), and the differences (shift to high field taken as positive, to low field negative) of the incremental shifts for the 8 and 9-methyl groups can be used as scaling factors to compare predicted with observed shifts. It can be seen from Figure 1 that the best fit is obtained when the plane containing carbon atoms 1, 2 and 3 is deflected down by approximately 20° from the plane containing carbon atoms 1, 3, 4 and 6, i.e. about 10° less than the maximum value. It therefore follows that the 10-methyl group in isopinocampnone must be near axial and in pinocampnone near equatorial.

S.A. Knight
S.A. KNIGHT
R.L. Erskine
R.L. ERSKINE

References:

- (1) McConnell, H.M., J Chem Phys, 1957, 27, 226.
- (2) Bhatt, M.V., Chem and Ind, 1959, 1452.
- (3) Bose, A.K., J Org Chem, 1955, 20, 1003, 1010.

Pages 1-2
Figures 1-2, (Serial Nos. 60/294-295 incl)
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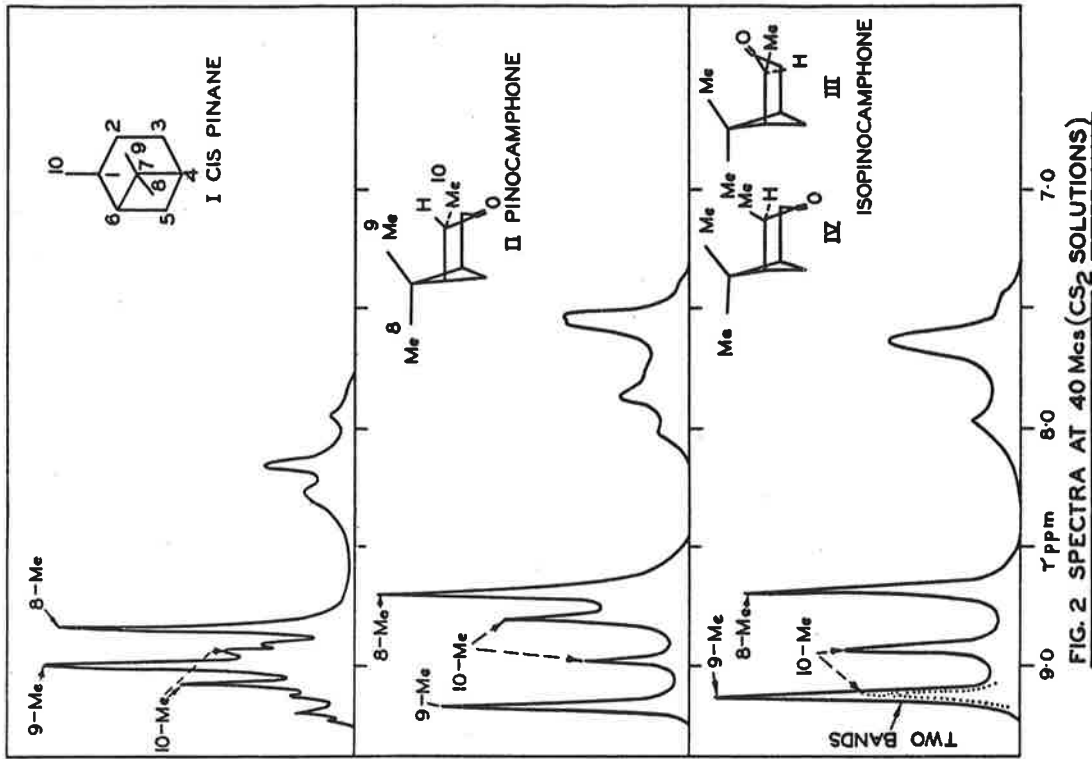


FIG. 2 SPECTRA AT 40 Mcs (CS₂ SOLUTIONS)

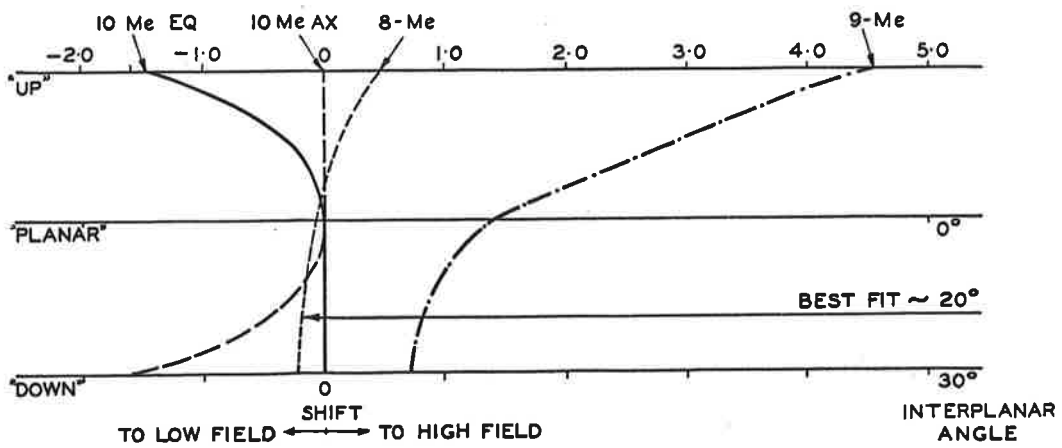


FIG. 1. DEPENDENCE OF $\Delta\sigma$ OF METHYL GROUPS 8, 9 & 10 ON CYCLOHEXANE RING CONFORMATION

CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA

GATES AND CRELLIN LABORATORIES OF CHEMISTRY

March 16, 1960

Dr. A. A. Bothner-By
Mellon Institute
440 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Bothner-By:

Tired from chasing "that certain spot" in the field and plagued by spinning sidebands, we've built a set of x, y and z current shims patterned after your design (NMR Letters, No. 9). The probe now stays put and natural abundance ^{13}C satellites have no spinning sideband companions. Without spinning, the methylene quartet of alcohol is sufficiently well resolved (each peak back to baseline) to suggest that for some low temperature work spinning could be dispensed with, greatly simplifying the usual Dewar apparatus. For those with similar problems and a day or so of free time the construction and installation details are outlined below.

The "figure 8" x and y coils and circular z coil of a set are wound consecutively on a slotted Lucite form and the leads are labeled with tabs. The wires are tied at each slot and where they cross through the form with No. 50 cotton thread. After removing the set, it is tied at additional points, coated with Epon Resin (828), baked (100°) and then pressed flat and reshaped as necessary against a pattern drawn on a piece of paper.

A set of horizontal and vertical cross hairs is accurately centered on each pole face with the aid of a level placed on the probe carriage, a ruler and a plumb line. The coils are aligned and fastened in place with Scotch tape. The leads are brought out to the stabilizer coil blocks and soldered to color coded hookup wire. The x and y coils are interconnected so that current passes through corresponding loops in the same direction while the z coils are connected in opposition. The leads to the control panel are fitted with pin jacks to facilitate reversing the direction of gradient correction.

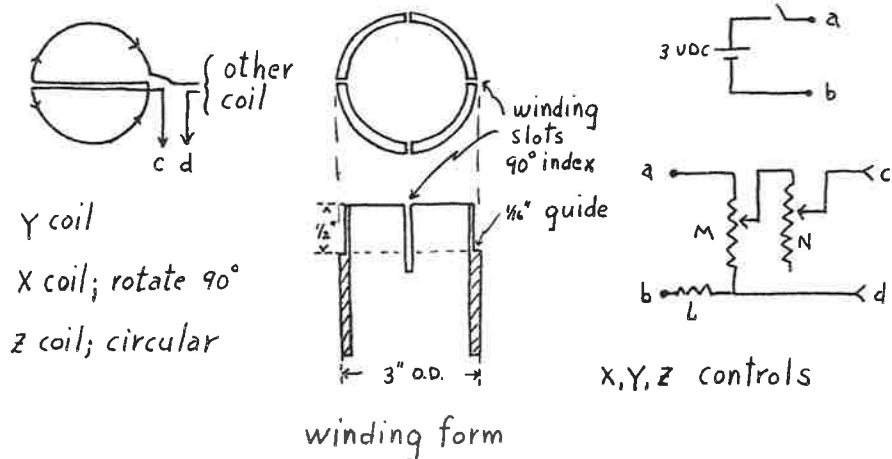
The probe is centered in the gap with spinning off and a narrow sweep field so that the signal on the scope does not shift when the x and y coarse controls are moved full range. The field trimmer is adjusted in the usual way with spinning and the y coarse control at midrange. Spinning is shut off and the x and z and finally the y controls are adjusted for maximum ringing. Precise field cycling is essential for maximum resolution.

The coil design is a compromise between the needs of our magnet and the available space behind the insulated pole face covers. The probe fits snugly but without binding or lateral pressure on the pole faces. The accompanying diagrams and chart are hopefully self-explanatory.

Sincerely yours,

Paul R. Shafer

PRS:pae



	turns (a)	M (b)	N (b)	L (b)
X	16	10 K	500	100
Y	8	10 K	100	100
Z	24	10 K	500	100

(a) No. 36 nylon insulated magnet wire. Allow ca. 20" leads, each coil.

(b) Ohms; M and N, wire wound pots.

Power: 3VDC from 8-1.5 VDC cells, series-parallel.

Drain: 6-8 ma, normal settings.

X, Y, Z controls

Dr. A. A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

RAH:1
Uppsala, March 20, 1960

Dear Sir:

In view of Dr. Reilly's letter in MELLON-NMR No 17 I wish to draw the attention to a closely related method of interpreting spectra, which may be understood in terms of perturbation theory (1).

Just as in the method of Reilly and Swalen (hereafter called method I), the analysis starts by obtaining in some way approximate values (screening constants δ_i^0 and coupling constants J_{ik}^0) for the NMR parameters. The NMR Hamiltonian with these values inserted (called H^0) is diagonalized on a computer and the eigenvalues and eigenvectors obtained. From here on the two methods follow different paths.

We may note that the correct Hamiltonian H depends linearly on all NMR parameters. It may thus be decomposed

$$H = H^0 + H^1$$

H^1 is of the same form as H but with all screening constants δ_i replaced by $(\delta_i - \delta_i^0)$ and all coupling constants J_{ik} by $(J_{ik} - J_{ik}^0)$. Now if our trial operator H^0 does indeed approximate H , then H^1 may be treated as a perturbation. The representation to be used for the perturbation calculations is that in which H^0 is diagonal. Corrected to first order (in $\delta_i - \delta_i^0$ etc.) the eigenvalue λ_k is then

$$\lambda_k^1 = \lambda_k^0 + \langle \gamma_k^0 | H^1 | \gamma_k^0 \rangle \quad /1/$$

where λ_k^0 and γ_k^0 are eigenvalue and eigenvector no k respectively as derived from H^0 . By taking the appropriate differences we obtain the 1st order approximation to the transition frequencies and finally these are compared with observed energies.

In order to see the relation to method I we may write /1/ in matrix form $\mathcal{A}^1 = \mathcal{A}^0 + A$; here A is the diagonal part of the matrix $U^{-1} H^1 U$. U is the unitary matrix built up from the eigenvectors of H^0 as column vectors. (Incidentally

RAH:2

it seems to me that in the formulae $UHU^{-1} = \mathcal{A}$ and $U^{-1} \mathcal{A}_{\text{exp}} U = H$ of Dr. Reilly's letter U and U^{-1} should be interchanged).

The relation between the two methods is now obvious. In first order the present method uses the similarity transformation, which is used to diagonalize H^0 also for transformation of the remaining part (H^1) of the true Hamiltonian. In method I on the other hand the inverse transformation is used to transform the experimental energy matrix. In both cases only the diagonal elements are retained. Both methods have the attractive feature that once approximate values of the NMR parameters are found one obtains linear equations relating the corrected values of these parameters to observed quantities.

Although I have not had much time to compare the two methods, some preliminary remarks on the differences between them may be added.

1/ The calculation of the matrix elements $\langle \gamma_k^0 | H^1 | \gamma_k^0 \rangle$ although trivial will in general be rather more lengthy than the calculation of the corresponding step in method I: $\sum_i U_{ni}^2 (\delta_i - \delta_i^0)$ exp. A computer program for this step in the present method is feasible however.

2/ The setting up of an experimental energy matrix \mathcal{A} as in method I is not necessary with the present method. In particular for a least squares fit this process may become time consuming. Moreover the present method works even if the initial assignment is extremely incomplete. For example in the 40 Mc/s spectrum of Thiophene (1) all parameters could be estimated from the moment method (2) and by use of data from substituted thiophenes (3) in particular the dideuterated compounds (1). However a first step in correlation of calculated and observed spectra was only made by considering the total width of the spectrum.

3/ In the present method there is an obvious way how to include higher order correction terms by means of 2nd and higher order perturbation theory. The resulting expressions

RMH:3

Will usually be too complicated to be useful in the interpretation of a particular spectrum. However, these terms could perhaps be useful in the study of the dependence of the spectrum on one or several parameters. For example the change of the spectrum for a particular molecule on slight variations in one or more chemical shifts due to solvent effects could possibly be best studied by use of the present method.

Such a study of the solvent dependence of shifts in some monosubstituted thiophenes is under way.

Sincerely Yours
Ragnar A. Hoffman
Ragnar A. Hoffman
Institute of Physics
UPPSALA, Sweden

REFERENCES:

1. Hoffman, R.A. and Gronowitz, S. Arkiv Kemi 15 45 (1959)
(For some reason this issue has not yet been distributed by the publisher, but reprints are available from the authors.)
2. Anderson, W.A. and McConnell, B.M. J. Chem. Phys. 26 1496 (1957)
3. Gronowitz, S. and Hoffman, R.A. Arkiv Kemi 13 279 (1958)

PS. I apologize for the bad typing. In order to have the letter mailed in time I had to write it at home with a sick type-writer.

THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

DEPARTMENT OF CHEMISTRY

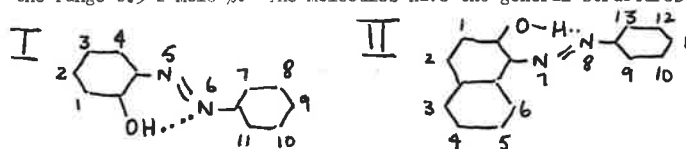
9 March, 1960

Drs. Paul C. Lauterbur
and Aksel A. Bothner By,
Mellon Institute,
4400 5th Avenue,
PITTSBURGH, Pa.

Dear Paul and Aksel,

I was very interested to read the letter of Porte, Gutowsky and Hunsberger in Mellon MR. No. 17. I would say that such results are similar to my own work here at U.B.C. which is the subject of a note in the Canadian Journal of Chemistry to appear in May 1960. In view of the difference in compounds used in my work it might be opportune to quote the figures that will appear.

The general approach here has been to measure nuclear shielding parameter relative to c_6H_{12} 0.5 mole % in CCl_4 as a solvent system. The substance under study is dissolved to about 1 mole % and the position of the -OH peak measured. The advantage of measuring nuclear shielding parameter for an intramolecularly bonded system in a dilute solution being that the entropy term due to dilution is not dominant in causing dissociation, as in inter hydrogen bonded molecules. One obtains consistent values of the chemical shift for the -OH peak which are not dilution dependent over the range 0.5-2 mole %. The molecules have the general structures below:-



In the table basic skeleton I or II is used to identify the compound, and the group and substitution position is referred to by the numbers indicated above. Column 2 of the table shows the chemical shifts as measured and Column 3 shows chemical shifts corrected for the large diamagnetic anisotropy of the rings by Pople's free electron model. The configuration of the molecule is taken to be that of

contd/-

transazobenzene or naphthalene and normal phenolic C-O and O-H distances and angles are used to locate the proton under study in the molecule. The comparison of the azobenzene and azonaphthalene -OH shifts is then put on a common basis.

The main feature of the results is the large shift 3 p.p.m. to low field in the naphthalene derivatives indicating a much stronger hydrogen bond. The electron withdrawing action of the larger naphthalene resonance system causes the β naphthol OH proton to be a much stronger acceptor, e.g. β naphthol is a stronger acid than phenol.

Within each series there is also correlation with hydrogen bonding strength since the di-hydroxy compound 2 has greatest shielding and is thus the weakest hydrogen bond in the azobenzene series. It is to be expected that the donor properties of one nitrogen will be affected to a small degree by the use of the other in a hydrogen bond. In the Shiffs base 5, the hydrogen bond is stronger because the difference in electronegativity of the nitrogen and the -CH= group increases the donor property of the nitrogen. Methyl substitution on the rings is apparently ineffective in changing the hydrogen bonding strength as measured by the nuclear shielding parameters.

In the -OH naphthalene derivatives substitution on the benzene ring only was studied. Chlorine substitution has little affect but the inductive effect of the methyl group appears to increase donor properties of the conjugated nitrogen. Several other features of these results will appear later but during the course of the study I received reprints from a third group of workers in Stockholm who have correlated proton shifts in chelated enolic forms of several molecules with the C=O stretch frequency (Forsen S, and Nilsson; M, Acta Chemica Scandinavica 13. p1383 (1959)).

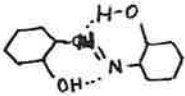
Yours sincerely,

Leonard W. Reeves

Leonard W. Reeves.

LWR:avh

TABLE I

Compound	$\{ \sigma_{C_6H_{12}} - \sigma_{OH} \}$ p.p.m.	$\{ \sigma_{C_6H_{12}} - \sigma_{OH} \}$ p.p.m. corrected	
I	- 11.03	- 9.98	1
	- 10.52	- 9.48	2
I 3,9 Dimethyl	- 11.00	- 9.95	3
I 3 Methyl	- 10.95	- 9.90	4
I 5. -CH= replaces -N=	- 11.40	- 10.37	5
II	- 14.26	- 13.06	6
II 9 Methyl	- 14.62	- 13.42	7
II 11 Methyl	- 14.12	- 13.92	8
II 9 Chloro	- 14.25	- 13.05	9
II 11 Chloro	- 13.97	- 12.77	10.