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PYRROLE STUDIES—XII[1]

THE AROMATIC CHARACTER OF 1-SUBSTITUTED PYRROLES

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Abstract—The NMR spectra of a series of 1-substituted pyrroles, -2,5-dimethylpyrroles, and -3,4-dimethylpyrroles are reported. The variations in the chemical shifts of the pyrrole ring protons and Me-substituents are discussed in relation to possible changes in the aromaticity of the pyrrole ring. Linear correlations with Hammett σ constants are obtained for both α and β protons and Me-groups of the 1-*p*-substituted aryl pyrroles and are interpreted in terms of a conjugative interaction of the *para* substituent with the benzene ring, but essentially an inductive interaction between the pyrrole nitrogen and aryl substituent. There is no evidence for an appreciable variation in the pyrrole ring current.

INTRODUCTION

PRIOR to 1957 it was generally accepted that the diene system of pyrrole resisted the normal Diels–Alder addition and, instead, underwent a Michael type addition to give α-substituted pyrroles.[2] Mandell and Blanchard[3] were the first to isolate a Diels–Alder adduct from the reaction of 1-benzylpyrrole and acetylene dicarboxylic acid, although under similar conditions neither 1-methylpyrrole nor pyrrole gave an adduct. A Diels–Alder adduct has since been postulated as an intermediate, although never isolated, in the reaction of pyrrole with dimethyl acetylenedicarboxylate[4,5] benzyne,[6] and hexafluorothioacetone.[7]

Mandell and Blanchard[3] originally suggested that the Diels–Alder adduct obtained was a result of the greater diene character of 1-benzylpyrrole as compared with 1-Me or unsubstituted pyrrole and that the presence of the bulky benzyl group required a greater energy to retain the coplanarity of the system with the consequent decrease in the aromatic character of the pyrrole ring. This suggestion was later retracted[8] and it was postulated that the Diels–Alder adduct from acetylene dicarboxylic acid was isolated purely as a result of its insolubility and its consequent inability to react further. In their attempt to isolate the Diels–Alder adduct Gabel[9]

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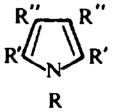
and Acheson[5] used 1-methoxycarbonyl-pyrrole but without success. The methoxycarbonyl substituent in the 1-position might be expected to produce a significant increase in the diene character of the pyrrole ring.

More recently stable adducts have been obtained from benzynes with both 1-alkoxycarbonyl and 1-alkylpyrroles.[10-12]

To determine the effect of the 1-substituent on the aromatic character of the pyrrole ring we have studied the NMR spectra of a series of 1-substituted pyrroles (I: R′ = R″ = H), -2,5-dimethylpyrroles (I: R′ = Me, R″ = H), and -3,4-dimethylpyrroles (I: R′ = H, R″ = Me). The shifts in the position of the signals due to the α and/or β hydrogens are considered in terms of the electronic effects in the pyrrole ring.



I

RESULTS AND DISCUSSION

The NMR spectra were recorded for dilute solutions in carbon tetrachloride to permit direct comparisons between chemical shifts in the three series of compounds studied. Experiments made at double and treble the concentrations used in this work showed only insignificant shifts (less than 0·3 c/s); the values recorded in Table 1 are effectively those at infinite dilution and are not affected by the well known self-association of aromatic solutes nor by the dimerization known to occur with pyrrole[13] and N-methyl pyrrole.[14]

The 1-substituted pyrroles showed characteristic A_2X_2 spectra for the pyrrole ring protons and chemical shifts were taken as those of the central peaks of the apparent triplets. The 2,5-dimethyl- and 3,4-dimethylpyrroles showed single unsplit peaks for both the pyrrole protons (half-width 1·5 c/s) and the Me protons (half-width 0·9 c/s) with no evidence of resolvable fine structure. The half-widths of the peaks suggest a Me-ring proton coupling no greater than 0·5 c/s in these compounds. 3,4-Dimethylpyrrole showed a clear doublet (J = 1·9 c/s) for the pyrrole ring protons through coupling to the N—H proton, which appeared as a broad unresolved singlet. The protons of the *para* substituted aromatic rings in the 1-aryl compounds appeared as the expected A_2B_2 patterns, or as single unresolved peaks where the chemical shift difference between the aromatic protons approached zero, and were not further analysed. The position of the other N-substituent resonances were not relevant to the present work and have not been recorded.

The chemical shifts of the pyrrole ring protons in the pyrrole, 2,5-dimethylpyrrole

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and 3,4-dimethylpyrrole series are recorded in Table 1 and those of the Me-protons in Table 2. Plots of the chemical shifts of the α and β pyrrole protons of the 1-arylpyrroles against Hammett sigma constants[15] are shown in Figs 1 and 2 and similar plots for the Me-group resonances are shown in Fig. 3.

TABLE 1. CHEMICAL SHIFTS OF PYRROLE RING PROTONS IN C/S FROM TMS AT 60 MC

Substituent	Pyrrole		2,5-Dimethylpyrrole	3,4-Dimethylpyrrole
	3,4H	2,5H		
H	365·3	398·8	330·9[b]	376·2[a]
Me	355·2	382·2[a]	330·3[c]	
Et	355·7	387·7	330·7	
CH_2Ph	360·8	390·3	338·3	
$C_6H_4NMe_2$-*p*	366·5	407·7	335·9	391·7[d]
C_6H_4OMe-*p*	368·6	$407{\cdot}5_5$	337·6	393·9
C_6H_4Me-*p*	369·8	413·1	338·3	398·0
Ph	371·4	416·7	340·0	400·2
C_6H_4Cl-*p*	$372{\cdot}4_5$	413·7	341·9	399·0
C_6H_4Br-*p*	372·5	413·5	341·5	398·8
$C_6H_4CO_2Et$-*p*	$374{\cdot}4_5$	421·8	342·7	406·6[e]
$C_6H_4NO_2$-*p*	381·9[f]	426·8[f]	346·6	408·2
1-Naphthyl			347·8	
4-Pyridyl	375·7	$424{\cdot}3_5$[g]	340·2	
CO_2Me	368·2	429·2	339·1	
COMe	370·3	430·8	340·9	413·5
COPh	$373{\cdot}6_5$	431·1	343·4	

[a] Taken from Hinman and Theodoropolus.[16]

[b] Hinman and Theodoropolus[16] gives 334·2.

[c] Hinman and Theodoropolus[16] gives 331·2.

[d] Amino-compound. Signal overlaps benzene hydrogen signals.

[e] Methyl ester.

[f] Measured in 20% $CDCl_3/CCl_4$.

[g] Signal overlaps pyridine hydrogen signals.

The chemical shifts of the α protons of the 1-substituted pyrroles cover a range of approximately 49 c/s, and within this range, the 1-arylpyrroles show a variation of 14 c/s with the change of *para* substituent, excluding the *p*-nitrophenyl compound which occurs at abnormally low field owing to the use of a mixed solvent system containing chloroform-*d*. The β protons cover a somewhat narrower range of 26 c/s and the variation for the 1-arylpyrroles is only 8 c/s. Both α and β protons show a reasonable linear correlation between chemical shifts and Hammett σ_P values for the *para* substituent (Figs 1 and 2) with considerably greater deviations from linearity for the α protons. The correlations are not significantly improved by

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using combinations of σ_I and σ_R values, and there is no evidence to suggest that σ^- values of strongly +M substituents are required to account for the effects of the nitro- and carbethoxy- substituents on the π-electron-rich pyrrole ring.[17]

Table 2. Chemical shifts of methyl group protons in c/s from TMS at 60 Mc

Substituent	2,5-Dimethylpyrrole	3,4-Dimethylpyrrole
H	130·0[a]	117·0[b]
Me	$128{\cdot}5_5$[c]	
Et	129·6	
CH_2Ph	125·3	
$C_6H_4NMe_2$-*p*	116·5	$119{\cdot}1_5$[d]
C_6H_4OMe-*p*	117·0	$119{\cdot}5_5$
C_6H_4Me-*p*	117·7	119·6
Ph	118·7	$120{\cdot}7_5$
C_6H_4Cl-*p*	118·8	120·1
C_6H_4Br-*p*	119·0	119·8
$C_6H_4CO_2Et$-*p*	120·2	$120{\cdot}9_5$[e]
$C_6H_4NO_2$-*p*	121·6	121·9
1-Naphthyl	111·3	
4-Pyridyl	120·2	
CO_2Me	140·2	
COMe	142·2	116·5
COPh	122·3	

[a] Hinman and Theodoropolus[16] gave 127·8.
[b] Taken from Hinman and Theodoropolus[16].
[c] Hinman and Theodoropolus[16] gave 126·0.
[d] Amino-compound.
[e] Methyl ester.

The shifts for the α protons of the 3,4-dimethylpyrroles and the β protons of the 2,5-dimethylpyrroles cover similar ranges (37 c/s and 17 c/s respectively) and the 1-aryl compounds also show a linear correlation between the chemical shift and Hammett σ_P values, (Figs 1 and 2) with slopes indentical to those of the corresponding protons in the pyrrole series, within the limits of experimental error. Plots of the chemical shifts of the α and β protons of the pyrrole series against those for the dimethylpyrrole series show an excellent linear correlation with slopes of unity. The 2,5-dimethyl substituents cause a characteristic upfield shift of approximately 30 c/s in the β proton resonances, while the 3,4-dimethyl substituents cause a smaller upfield shift of approximately 15 c/s in the α proton resonances. Thus the α proton, which is twice as sensitive to N-substituent effects as the β proton, is only half as sensitive to the effect of Me-substitution at the adjacent carbon atom.

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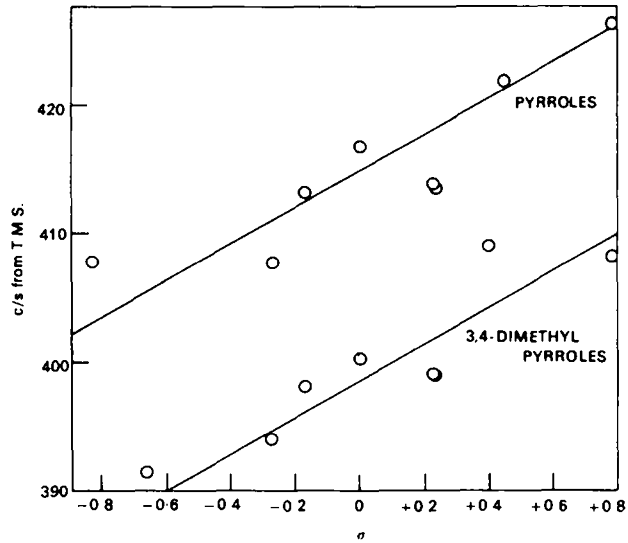

FIG. 1. α-Proton resonance signals for 1-substituted pyrroles and 1-substituted 3,4-dimethylpyrroles.

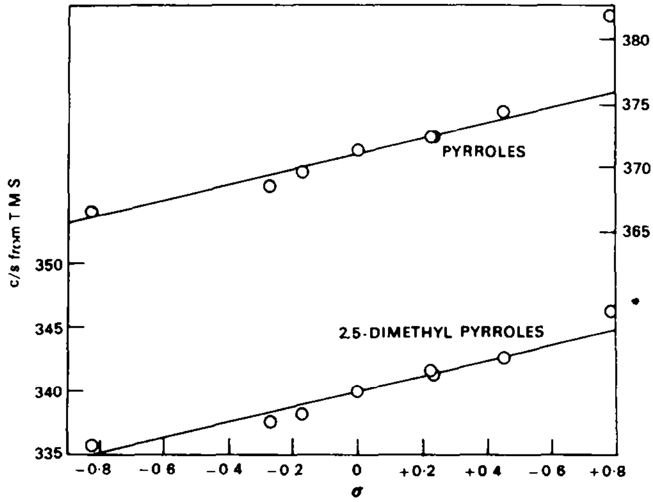

FIG. 2. β-Proton resonance signals for 1-substituted pyrroles and 1-substituted 2,5-dimethylpyrroles.

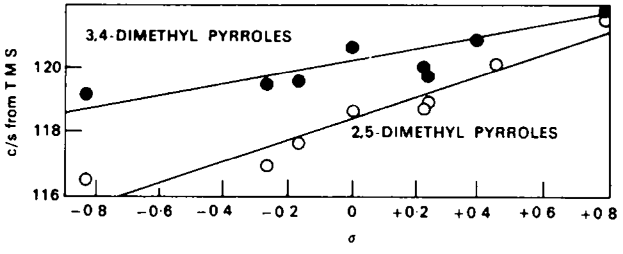

FIG. 3 α and β-Me resonance signals.

The correlation between the Me-group resonances and Hammett σ_p values is significantly poorer, probably because of the smaller shifts involved (5·1 c/s for the α Me-groups and only 2·8 c/s for the β Me-groups; Fig. 3.) There is a fair linear correlation between the chemical shifts of the α and β Me-groups, with the α Me-groups showing approximately twice the shift of the β Me-groups, in agreement with the results obtained for the corresponding pyrrole ring protons.

An extended plot of α proton against β proton resonances for the full series of compounds listed in Table 1 is shown in Fig. 4. It is clear that the linear correlation

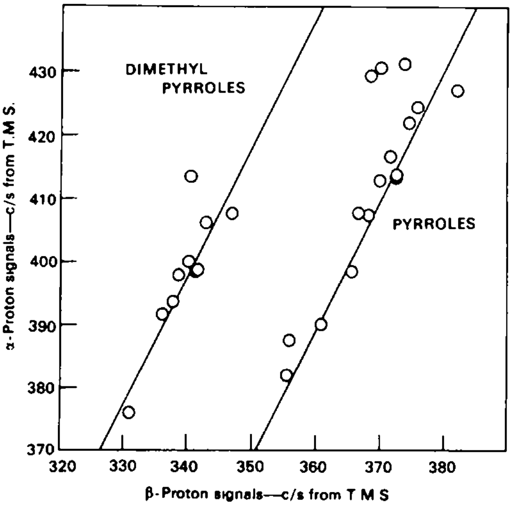

FIG. 4 Plot of α-proton resonance signals against β-proton resonance signals.

between the shifts of these protons is not limited to the 1-aryl compounds and that significant deviations from linearity occur with 1-substituents containing a carbonyl group, where the α protons show a characteristic low field shift through their proximity to the anisotropic carbonyl group.

The correlations obtained between α and β proton and Me-group resonances and Hammett σ_p values are a clear indication of a substituent effect transmitted to the pyrrole ring, but give little indication of the way in which this effect is transmitted or of the effect of the substituent on the aromatic character of the pyrrole ring. The relationship between chemical shift and aromatic character, defined as the ability to sustain an induced ring current,[18] is presently the subject of considerable controversy, particularly for the heterocyclic compounds thiophen, furan and pyrrole,[19-22] and even the magnitude of the chemical shift due to ring currents in benzene is in doubt. From calculations made by Pople,[23-24] almost one third of the chemical shift differences in benzene usually ascribed to ring current effects may be due to local paramagnetic contributions from the ring carbon atoms, and even the existence of a ring current has been questioned.[25]

In the following discussion we adopt the view that a ring current in pyrrole contributes significantly to the chemical shifts of ring protons and substituents and that the magnitude of this effect bears a direct relationship to the aromaticity of the pyrrole ring. From calculations based on the chemical shifts of ring protons and Me-groups, pyrrole has been assigned 59% of the aromatic character (or ring current) of benzene,[20] although the significance of this estimate is doubtful because of the difficulty in selecting a suitable non-aromatic standard for comparison. Fortunately, the exact magnitude of the ring current effect is not of great importance in the present series of compounds. We assume in the following discussion that the maximum ring current effect in pyrrole is less than the maximum usually attributed to the benzene ring (117 c/s at 60 Mc. for the ring protons) and that the angular dependence of this effect is given approximately by the point dipole expression,[26] with the magnetic dipole located at the centre of the ring and at the right angles to the plane of the ring.

Other important investigations of the NMR spectra of substituted pyrroles have been concerned with estimates of aromatic character,[20, 27] Me-substitution,[16, 28] dimer formation,[13, 14] protonation[29] and coupling constants[30, 31] but no systematic investigation of substituent effects has been reported.

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The following factors may be considered as possible sources of the variation in chemical shifts observed in the 1-aryl substituted compounds:

(a) variation in the ring current of the pyrrole ring with N-substituent,
(b) a conjugative or non-conjugative transfer of electronic effects to the pyrrole ring via the pyrrole nitrogen,
(c) an electrostatic field effect of the N-substituent dipole transmitted through space,[32,33]
(d) a reaction field effect transmitted by polarization of the solvent molecules,[32]
(e) variation in the ring current of the 1-Ph group with substituent.

Possibilities (c), (d) and (e) can be excluded as major mechanisms for the substituent effects by considering the magnitudes of shifts involved. It is inconceivable that a variation in the ring current of the substituted Ph-ring could be sufficient to produce the observed chemical shift differences. Assuming a planar conformation for the 1-phenylpyrroles, the maximum ring current contribution to the chemical shifts of the β and α protons are 8·5 c/s and 29 c/s respectively, and the values recorded for pyrrole and 1-phenylpyrrole (Table 1) suggest 6 c/s and 18 c/s as the experimental figures for the shifts of the β and α protons due to the presence of the aromatic ring. Clearly, a variation of more than 50% of the ring current in the aryl ring would be required to produce the observed shifts, and experiments on the cumulative effects of electron donating substituents attached to an aromatic ring,[34,35] have demonstrated that the ring current contribution is little affected.

Similarly, according to current theoretical treatments,[32,33] the electrostatic fields along the C—H bonds of both α and β protons due to an electrostatic dipole localized at the mid-point of the bond between the substituent and the aromatic ring would be responsible for less than 1 c/s variation in the chemical shifts of these protons. The reaction field effect, transmitted by polarization of solvent molecules, should also produce only minor variations in the chemical shifts of the α and β protons, and further, the direction of this effect (parallel to the dipole moment vector) would be such that the α protons should be shielded and the β protons deshielded.[32]

The two effects (a) and (b) are interrelated. A conjugative transfer of electronic effects from the substituent to the pyrrole ring must be accompanied by some modification of the pyrrole ring current and these two effects should operate in different directions. Thus the *p*-carbethoxy substituent could produce a downfield shift of both α and β proton and methyl group resonances by a conjugative reduction of electron density at the α and β carbon atoms. The resultant decrease in the electron density in the pyrrole ring must result in a lower ring current contribution to the chemical shifts of these protons, and hence an opposing upfield shift. The observed range of chemical shifts would be accommodated by a variation of about 0·03 in the π-electron density at the α carbon atom, and a somewhat smaller variation at the β carbon atom[36,37] and this change in charge distribution would have a negligible

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effect on the ring current in the pyrrole ring. Since the observed shifts are paramagnetic with electron withdrawing substituents, and diamagnetic with electron donating substituents, we conclude that the major effect is due to a variation in the π-electron density at the α and β carbon atoms of the pyrrole ring.

The correlation between Hammett σ_P values and chemical shifts could imply direct conjugation between the Ph substituent and the pyrrole ring, or a primarily inductive transfer of substituent effects from the substituted aromatic ring of the pyrrole nitrogen, with a consequent variation in the effective electronegativity to this atom. Simple Hückel M.O. treatments indicate that both a conjugative transfer and an essentially inductive transfer of substituent effects would produce greater variations in the π-electron density at the α carbon atom than the β carbon atom. The effect of increasing the effective electrongativity (coulomb integral) of the pyrrole nitrogen on the π-densities in the pyrrole ring, with constant C—N resonance integral and neglect of overlap, is shown in Table 3. The predicted variations agree well with the experimental ratio of approximately 2:1 for the chemical shifts at the α and β positions.

TABLE 3. π-ELECTRON DENSITY AND N ELECTRONEGATIVITY IN THE PYRROLE RING (HÜCKEL M.O.)

Coulomb integral N[a] h	β_{C-N}[b]	π-Density C-2	C-3
0·000	1	1·200	1·200
0·500	1	1·135	1·177
1·000	1	1·085	1·156

[a] $\alpha_N = \alpha_C + h\beta_O$
[b] $\beta_{C-N} = \beta_{C-C} = \beta_O$

Linear Hammett σ value relationships for chemical shifts have been interpreted as primarily conjugative effects on the π-electron density for phenols,[38] anisoles,[39] anilines,[40–42], toluenes,[43] substituted benzenes,[44] purines,[45] 2-methyl benzothiazoles,[46] dimethylanilines,[47] benzaldehydes,[48] and heterocyclic analogues of cinnamic acid,[49] but similar correlations for phenylacetylenes[50] and ethylbenzenes[51] have

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been interpreted as a conjugative interaction of the substituent with the aromatic ring and inductive transfer from the ring to the side chain. The latter mechanism for the transfer of substituent effects provides an adequate explanation for the present series of compounds.

If it is assumed that the Ph-ring and the pyrrole ring are essentially coplanar in the pyrrole and 3,4-dimethylpyrrole series, and that the resonance interaction between the two rings is at a maximum for these compounds, then the conjugative transfer of substituent effects should then be greatly reduced in the 2,5-dimethylpyrroles, where steric repulsion between the α methyl groups and the *ortho* hydrogens of the benzene ring must result in a conformation in which the interplanar angle of the pyrrole ring and Ph-ring approaches 90°. This conclusion is supported by the chemical shift data where the α-Me groups for the 2,5-dimethylpyrroles, are shifted to higher fields by the presence of the 1-Ph substituent (Table 2), whereas the α protons in the pyrrole and 3,4-dimethylpyrrole series show the expected low field shift with 1-Ph substituents, implying that the Me-groups in the 1-phenyl-2,5-dimethylpyrrole series lie in the shielding region of the aromatic ring. Since the efficiency of the conjugative interaction between the two rings is a function of the N—C (Ph) overlap integral which has an approximate $\cos^2 \theta$ dependence on the interplanar angle θ, transfer of substituent effects by conjugation between the phenyl ring and the pyrrole ring should be very small for the 2,5-dimethylpyrroles.

However, the experimental results do not entirely support such an effect. Clearly the transmission of substituent effects to the β protons in the pyrrole and 2,5-dimethylpyrrole series is not affected by the change in conformation. Further, the chemical shift differences of approximately 19 c/s between the α protons in pyrrole and 1-phenylpyrrole; and 3,4-dimethylpyrrole and 1-phenyl-3,4-dimethylpyrrole are in better agreement with the values calculated for a freely rotating phenyl group (19 c/s for $\Delta\chi = -59{\cdot}7 \times 10^{-6}$ cm^3/mole) than for a planar conformation (29 c/s). The experimental results can be adequately explained only if it is assumed that the transmission of the substituent effects between the substituted Ph-rings and the pyrrole nitrogen is essentially inductive, and therefore invariant with the interplanar angle between the rings, which are probably freely rotating in the pyrrole and 3,4-dimethylpyrrole series, just as the two Ph-rings appear to be in biphenyl.[52]

On this model the observed variations in chemical shifts may be correlated with the variations in π-electron density at the α and β carbon atoms of the pyrrole ring through the varying electronegativity of the pyrrole nitrogen. We conclude that there is no evidence for appreciable variations in the ring current of the pyrrole ring with varying 1-substituents, and therefore no appreciable variation of the aromaticity of the ring as defined above, although the reactivity may well be affected by variations in π-electron density.

EXPERIMENTAL

Materials. All the 1-substituted pyrroles were prepared by standard methods and their preparation has been reported elsewhere.[53] The compounds were distilled or recrystallized immediately before use.

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NMR measurements. NMR spectra were determined in CCl_4 soln on a Varian D.P.60 spectrometer with TMS as internal standard. Calibration was by the usual side-band technique, using a Muirhead-Wigan D-890-A audio oscillator. The chemical shifts were recorded for dilute solns (less than 0·05 M) and the values are the average of 6–10 scans; the values given are believed to be accurate to ±0·1 c/s. 1-(*p*-nitrophenyl) pyrrole was insufficiently soluble in CCl_4 and the values for this compound were recorded for a 0·03 M soln in CCl_4 containing $CDCl_3$