Synthesis and Stereochemistry of Reissert Compounds from Benzothiazole

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Benzothiazole Reissert compounds **1–5** were synthesized, characterized and alkylated to produce **6–9**. Conformational analysis of **2** by the use of high resolution (400 MHz) variable temperature NMR spectroscopy indicated that the *Z* to *E* amide conformer ratio is 79:21 (±3%) in $CDCl_3$ at 213 K (−60 °C) and 57:43 (±3%) in $C_6D_5CD_3$ at 213 K. Aromatic solvent induced shifts were employed to determine the distribution of rotamers and indicated that the alkylated benzothiazole Reissert compound **8** existed in only the *Z* amide conformation. Hindered aryl–carbonyl rotation was also detected in the Reissert compounds.

Introduction

Reissert compounds were first synthesized at the turn of this century by Arnold Reissert.[2] Since then a variety of heterocyclic bases have been used in the syntheses of Reissert compounds.[3] The most successful procedure is the very convenient two-phase method[3,4] which uses methylene chloride and water with or without a phase-transfer catalyst and agitation for reaction between potassium cyanide and the acylium complex formed from the heterocycle and the acid chloride.

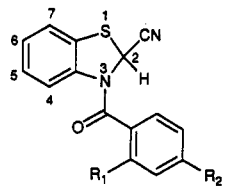
This technique fails in the case of five-membered fused heterocycles, e.g., benzothiazole and benzimidazole. The use of trimethylsilyl cyanide (TMSCN) as the nitrile source in a homogeneous organic medium gave excellent yields for Reissert compounds from isoquinoline and quinoline.[5] This technique was used to synthesize the first pyridine Reissert compound[6] and some fused five-membered systems including benzothiazole.[7] Recently, the synthesis of the first bis Reissert compound from benzimidazole[8] and the first synthesis of a benzimidazole Reissert compound from an acid chloride were reported.[9]

Our interest in the use of benzothiazole as the heterocyclic precursor to Reissert compounds stems from the interesting chemistry of these compounds[10] and the role that the benzothiazole moiety plays when catenated in a chain.[10] Thiazoles and their benzo derivatives have diverse uses such as antibiotics,[11] flavoring agents for foods,[12] anti-inflammatory agents,[13] anthelmintic and fungicides,[13] herbicides,[14] in colorimetric estimation of phenols,[13] and sensitizing dyes in silver photography.[15] The benzothiazole nucleus has been used to provide a carbonyl equivalent in the synthesis of unsaturated aldehydes and ketones resulting in high yields of those synthons.[16] By the use of Reissert compound chemistry, we have synthesized novel polymers,[17–21] some involving benzothiazole Reissert compounds. It was essential, therefore, to synthesize model compounds and study their reactions and stereochemistry.

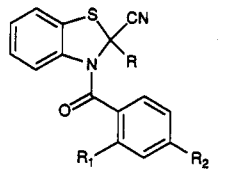
In this paper, we report the synthesis of some new Reissert compounds from benzothiazole and their alkylation via the conjugate carbanions. The stereochemistry of these compounds is also discussed.

Results and Discussion

A. Synthesis. Uff[22] reported the synthesis of a few Reissert compounds from benzothiazole and para-substituted benzoyl chlorides. We now report the synthesis of benzothiazole Reissert compounds **1–5** in quantitative



1: R_1 = Cl, R_2 = H
2: R_1 = Me, R_2 = H
3: R_1 = H, R_2 = H
4: R_1 = H, R_2 = Me
5: R_1 = H, R_2 = t-Bu



6: R = Me, R_1 = Cl, R_2 = H
7: R = Me, R_1 = Me, R_2 = H
8: R = Me, R_1 = H, R_2 = H
9: R = p-ClC$_6$H$_4$CH$_2$, R_1 = R_2 = H

yields utilizing *o*-chlorobenzoyl chloride, *o*-toluoyl chloride, *p*-toluoyl chloride, *p-tert*-butylbenzoyl chloride and benzoyl chloride by the use of trimethylsilyl cyanide as the nitrile source in methylene chloride (Table I). Some of these Reissert compounds were alkylated via the corre-

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Table I. Benzothiazole Reissert Compounds and Their Alkylation Products

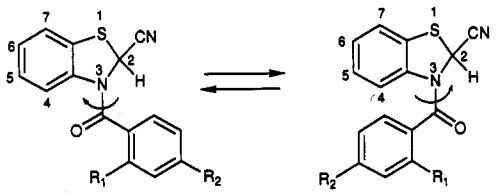
compd	yield (%)	mp (°C)	elemental analyses[a] (%) C	H	N
1	100	183.5–185.0[b]	59.90 (59.90)	2.99 (3.02)	9.35 (9.32)
2	100	152.5–154.0[c]	68.53 (68.55)	4.32 (4.32)	10.01 (10.00)
3	100	127.0–128.5[d,e]			
4	100	153.4–154.2[d,f]			
5	100	131–132[d]	70.71 (70.77)	5.66 (5.63)	8.67 (8.69)
6	85	163.8–164.8[d]	61.10 (61.04)	3.57 (3.52)	
7	85	110.8–111.8[d]	69.45 (69.36)	4.81 (4.79)	
8	100	112–115[d]	68.68 (68.55)	4.30 (4.31)	
9[g]	100	172–174[h]	67.66 (67.59)	3.92 (3.87)	7.17 (7.17)

[a] Value in parentheses is the calculated number. [b] Recrystallized from 3:7 *N,N*-dimethylformamide/ethanol. [c] Recrystallized from 1:18 *N,N*-dimethylformamide/ethanol. [d] Recrystallized from 95% ethanol. [e] Lit.[22] 139–141 °C. [f] Lit.[22] 158–160 °C. [g] S: 8.21 (8.20). [h] Recrystallized from 100% ethanol.

sponding carbanions (NaH/dimethylformamide) forming **6–9** in very high yields (Table I).

B. NMR Studies of Stereochemistry of Reissert Compounds. The investigation of benzothiazole Reissert compounds from ortho-substituted benzoyl chlorides was motivated by a very peculiar ^{1}H NMR spectrum (Figure 1) obtained for a solution of **3** in $CDCl_3$. The 4-proton signal, located at 6.75 ppm, was unusually broad (ca. 0.26 ppm at ambient temperature). Selective proton decoupling and the fact that it did not exchange with D_2O yielded confirmation of its assignment as the 4-proton. The broadness of the signal is attributed to the slow interconversion of amide rotamers relative to the NMR time scale. Conformational analysis of isoquinoline Reissert compounds and alkylated derivatives has been dealt with in depth by Gibson.[23-25] This phenomenon has been discussed thoroughly in a treatise.[26]

Portrayed below is the conformational isomerism about the amide C–N bond.



The 4-proton experiences different magnetic environments in the two conformations *E* and *Z*. *E* is the conformation where the carbonyl C=O bond is trans to the nitrile and *Z* is the conformation where the C=O is cis to the CN moiety. At low temperatures, the interconversion is slow and there are two distinct signals for the 4-proton in the NMR. At intermediate temperatures, the interconversion is more rapid and the two peaks broaden and a smeared resonance is seen. At high temperatures, the rate of interconversion is fast and only one peak is observed, corresponding to the time-averaged contributions of *E* and *Z*.

Further, when the *low temperature* (213 K) NMR spectrum of **2** was obtained in either $CDCl_3$ (Figure 2) or $C_6D_5CD_3$, *three* signals were obtained in the methyl region

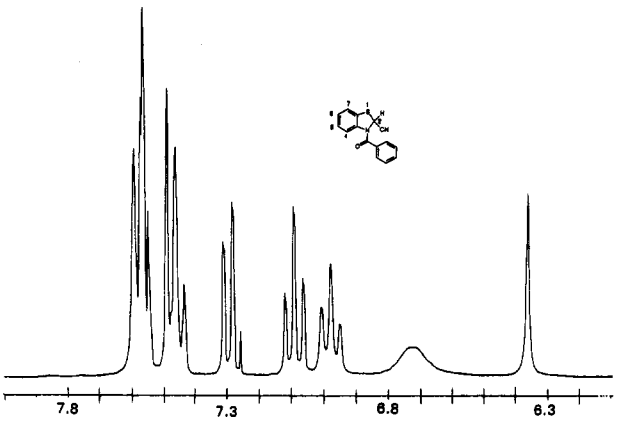


Figure 1. 270-MHz ^{1}H NMR spectrum of **3** in $CDCl_3$ at 298 °K.

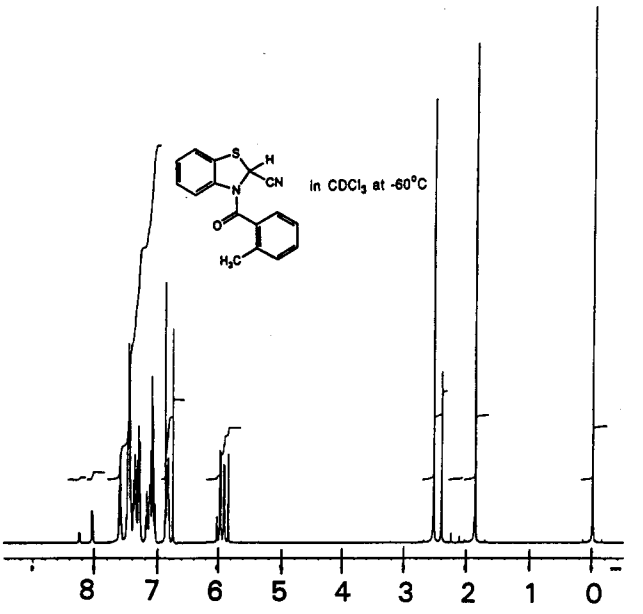


Figure 2. 400-MHz ^{1}H NMR spectrum of **2** in $CDCl_3$ at 213 °K.

of the NMR spectrum. These arise due to the freezing out of the four possible conformational isomers as shown in Scheme I.

These conformational isomers arise due to the restricted rotation around (a) the N–C=O bond and (b) the aryl–C=O bond. The restricted rotation due to a gives rise to *E* and *Z* isomer pairs and that due to b gives rise to syn and anti isomer pairs. When the methyl and nitrile groups are in opposite spatial directions, i.e., the dihedral angle is greater than 90° and less than 180°, that conformation is the anti. When the dihedral angle is between 90° and 0°, that is the syn conformation.

The aroyl group in **2** has a *local asymmetry* in that there is a methyl group at the 2-position and a proton in the 6-position. This gives rise to *four conformers* when all rotameric interconversion is frozen at low temperatures; *unequal* proportions of conformers are obtained. Apart from these conformers, we might expect additional rotamers from conformational changes at other junctures in the molecule, namely the nitrogen inversion[27] and the ring inversion involving C2, N, and S in a concerted movement.[28] The energy barriers for the latter two modes

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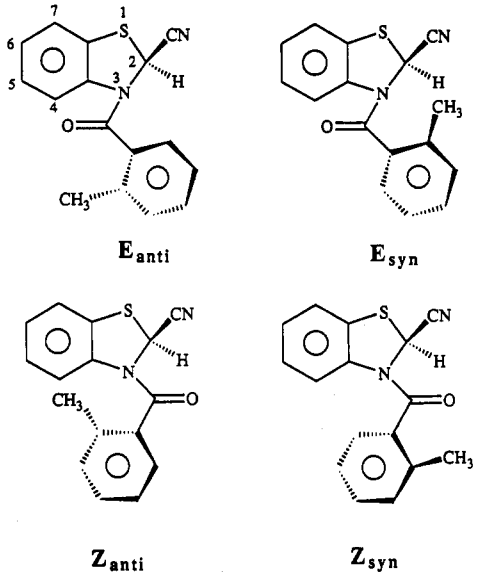
Scheme I. Conformational Isomers of 2 (only one enantiomer shown).



are known to be quite low (ca. 1–2 kcal/mol) and we thus expect the amide isomerism to be the *dominant* one observed.

Analysis of the four conformers (Scheme I) on the basis of magnetic and electronic environments of the different protons points to the following situation. Molecular mechanics calculations[29] have established several points. In all four conformers, the cyano group is axial in the lowest energy state. The amide group is nearly coplanar (deviation 5–10°) with the benzo ring in all cases. Also in each case, the aroyl ring assumes an angle of 60–90° with respect to the C=O plane. For the *E* form, since the N–C=O group and attached atoms are planar or nearly so, H-4 lies in the nodal plane of the π system of the amide carbonyl linkage and thus is deshielded. The H-2 proton, on the other hand, is so situated spatially that it lies in the shielding region (π-cloud) of the phenyl ring. The reverse is true for the *Z* form. Within either the *E* or the *Z* amide isomer, the syn rotamer has the methyl group placed within the deshielding region of the cyano group. This tends to make the methyl group appear at low field; this was diagnostic in assigning the observed signal to that rotamer. Aryl methyl protons typically resonate at ca. 2.27 ppm.[30] A downfield shift (relative to δ 2.27) can therefore be ascribed to the syn form. Conversely, for the E_{anti} and the Z_{anti} conformers, the methyl group is expected to be shielded because the methyl protons lie in the shielding zone of the aromatic ring of the benzothiazole moiety.

H-4 has only one vicinal proton and therefore will appear as a doublet with a coupling of ca. 6.5–8 Hz. H-2 on the other hand can appear only as a singlet. Further, each signal corresponding to H-2 and H-4 at ambient temperature is *expected* to split into a maximum of four signals (barring accidental overlap) at a lower temperature, the relative integrations being indicative of the amounts of conformers frozen out.

Table II lists the shifts and percentages pertaining to the various rotamers of **2** at 213 K in $CDCl_3$ based on the

Table II. NMR Data and Assignments for 2 in $CDCl_3$ at 213 K

proton	Z_{anti}	Z_{syn}	E_{anti}	E_{syn}
	δ (conformer population, %)[a]			
H-2	6.87 (42.9)	6.74 (34.7)	5.84 (15.8)	6.02 (6.7)
H-4	5.96 (43.9)	5.90 (37.3)	8.03 (14.3)	8.24 (4.4)
	Z_{anti}	$(Z+E)_{syn}$		E_{anti}
CH_3	1.87 (42.0)	2.53 (41.9)		2.40 (16.1)

[a] ±Three percent error in integration values.

H-2, H-4, and the methyl signals. On the basis of the above logic, we assigned the two downfield singlets (Figure 2) for H-2 (6.87 and 6.74 ppm) to the *Z* form and the upfield signals, 5.84 and 6.02 ppm, to the *E* form.

Steric hindrance by the methyl group dictates that the peak with a larger integration within the *Z* form be Z_{anti}; therefore the H-2 peak at 6.87 ppm with an overall integration of 42.9% was ascribed to Z_{anti}. The Z_{syn} population is 34.7%, E_{anti}, 15.8%, and E_{syn}, 6.7% in $CDCl_3$. The E_{anti} and the Z_{anti} conformer resonances for H-2 occur 1.03 ppm apart.

For H-4, the *E* form is more deshielded than the *Z* form and therefore the two H-4 doublets at 8.24 ppm (J = 8.1 Hz) and 8.03 ppm (J = 8.2 Hz) are representative of the *E* form. Steric hindrance by the methyl group, as indicated by molecular mechanics calculations,[29] dictates that the peak with the larger relative conformer population within the *E* form be E_{anti}; therefore the H-4 peak at 8.03 ppm with an overall integration of 14.3% was ascribed to E_{anti} and the H-4 peak at 8.24 ppm with an integration indicative of 4.4% conformer content was assigned to E_{syn}. The H-4 peaks at 5.96 ppm (J = 8.1 Hz) and 5.90 (J = 8.2 Hz) are of the *Z* form. The integration ratios help in *consolidating the assignments*. Thus the H-4 peak at 5.96 ppm with an integration of 43.9% must belong to the Z_{anti} conformer and the H-4 peak at 5.90 ppm, integration 37.3%, is indicative of the Z_{syn} conformer. The Z_{syn} and the E_{syn} conformer resonances for H-4 occur 2.34 ppm apart; this is consistent with the close proximity of the H-4 to the deshielding carbonyl moiety in E_{syn} and the shielding aromatic ring of the aroyl moiety in Z_{syn}.

One of the methyl resonances occurs at 1.87 ppm. This peak is shielded ca. 0.4 ppm compared to a normal aryl methyl and represents the Z_{anti} form in which the aryl methyl is expected to be most shielded by the fused aromatic ring π-cloud. The methyl peak at 2.53 ppm is ascribed to the E_{syn} and Z_{syn} conformers since the methyl is deshielded by the nitrile; integration analysis indicates that the *combined conformer population* is 41.9%. The remaining methyl peak at 2.40 ppm represents the E_{anti} conformer and its relative integration is in close agreement with that of analogous assignments for H-2 and H-4. This overall analysis gives a 79:21 (±3%) *Z*/*E* ratio of conformer populations. Molecular mechanics calculations[29] agree quite well with the experimental results, predicting a 4:1 *Z*/*E* ratio (ΔG ca. 1.0 kcal/mol).

The ASIS (aromatic solvent induced shifts)[31] technique consists of determining the NMR spectrum of the compound of interest in CCl_4 or $CDCl_3$ and then in an aromatic solvent such as $C_6D_5CD_3$. If the subtraction of the shift of a protonic moiety in the $C_6D_5CD_3$ NMR spectrum from the corresponding one in $CDCl_3$ gives a *large positive value*, i.e., an *upfield* shift in the aromatic solvent, then that

(29) PC Model Serena Software, version 2.0, P.O. Box 3076, Bloomington, IN 47402.

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Table III. NMR Data and Assignments for 2 in $C_6D_5CD_3$ at 213 K

proton	Z_{anti}	Z_{syn}	E_{anti}	E_{syn}
	δ (conformer population, %)[a]			
H-2	5.64 (28.6)	5.50 (28.6)	4.05 (35.7)	4.60 (7.1)
CH_3	1.52 (27.2)	2.22 (30.0)	2.03 (34.7)	2.38 (8.1)
	$Z_{(syn + anti)}$		E_{anti}	E_{syn}
H-4	5.70 (58.1)		8.11 (35.8)	8.51 (6.2)

[a] ±Three percent error in integration values.

moiety is deemed trans to the amide carbonyl oxygen; the cis substituent also may give upfield shifts but *only up to half the magnitude* of the trans group.[32,33]

Table III lists the chemical shifts and percentages pertaining to the various rotamers for the NMR spectrum of 2 at 213 K in $C_6D_5CD_3$.

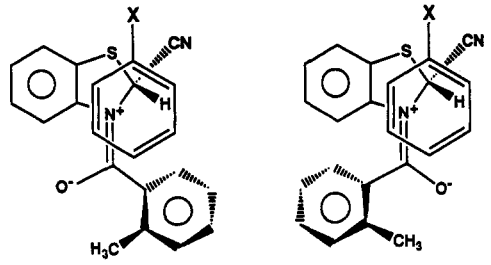
When the solvent is changed to $C_6D_5CD_3$ (Table III), there is a change in the ratio of the conformer populations of 2. The H-2 resonances have moved *upfield* to a considerable extent. This has been reported by Hatton and Richards[32] and Moriarty[33] for amides and lactams, respectively. The same is not true for H-4; in fact both the conformers of the *E* form, which are still expected to exhibit resonances at lower fields, are more deshielded *than in* deuterochloroform. For H-2, the two *upfield* resonances are at 4.05 and 4.60 ppm and the *downfield* resonances are at 5.50 and 5.64 ppm. Compared to the shifts of H-2 in deuterochloroform, where the two *most upfield* H-2 resonances are at 5.84 and 6.02 ppm, there is certainly a shielding effect of the solvent evident. The H-2 peak at 4.05 ppm with a relative integration of 35.7% is assigned as the E_{anti} conformer and the H-2 peak at 4.60 ppm to the E_{syn} conformer with a relative integration of 7.1%. For H-2, the Z_{syn} and the Z_{anti} conformers are again expected to be deshielded, although not as much as in the deuterochloroform, and the H-2 peaks at 5.50 and 5.64 with equal relative integrations of 28.6% are assigned to those conformers. For H-4, the E_{anti} and the E_{syn} conformers are expected to be the most deshielded ones. The H-4 peaks at 8.11 and 8.51 ppm with relative integrations of 35.8 and 6.2% are assigned to E_{anti} and E_{syn}, respectively, consistent with the integrations of the various conformer assignments based on H-2. The two *upfield* methyl resonances at 1.52 (27.2%) and 2.03 (34.7%) ppm are assigned to the E_{anti} and the Z_{anti} conformers since the methyl group is anti to the nitrile and, as explained earlier, is shielded by the aromatic ring of the benzothiazole moiety; Z_{anti} is more upfield than E_{anti} due to the closer proximity of the methyl protons to the shielding region of the aromatic ring. Both of these methyl signals are shielded, by 0.35 and 0.37 ppm, respectively, in deuterotoluene, relative to deuterochloroform. The remaining methyl peaks at 2.22 (30.0%) and 2.38 ppm (8.1%) are indicative of the Z_{syn} and the E_{syn} conformers; these too are shielded relative to deuterochloroform, by 0.31 and 0.15 ppm, respectively. The *Z*/*E* conformer population ratio for 2 is 57:43 (±3%) in deuterotoluene. This *lowering* in *Z*/*E* conformer ratio from 79:21 when the solvent is changed from $CDCl_3$ to deuterotoluene is rationalized as follows. Although steric interactions are minimized in the *Z* isomer, the overall dipole moment of the molecule is highest in the *Z* form when the dihedral angle between the CN and the C=O approaches 0. *The E form has the lower dipole moment and thus is more stabilized in a nonpolar solvent like toluene while the Z form is more stabilized in a polar solvent like chloroform.*

Table IV. ASIS Values for Different Conformers of 2 at 213 K

	$\Delta(E_{anti})$,[a] ppm	$\Delta(E_{syn})$, ppm	$\Delta(Z_{anti})$, ppm	$\Delta(Z_{syn})$, ppm
H-2	+1.79	+1.42	+1.23	+1.24
H-4	−0.08	−0.27	+0.26	+0.20

[a] $\Delta(E_{anti})$ means the difference of shifts for the E_{anti} conformer when the solvent is changed form $CDCl_3$ to $C_6D_5CD_3$.

Table IV summarizes the ASIS values for each conformer based on these assignments. It is evident from Table IV that H-2 is much more sensitive to a change in solvent than H-4. In all the conformations, H-2 is differentially *shielded* to large extents in deuterotoluene relative to the deuterochloroform but particularly in the conformers of the *E* form. The upfield shifts of H-4 in the *Z* isomer are consistent with the H-2 results. Hatton and Richards[32] have reported analogous upfield shift for both the cis and trans forms of the amides that they studied. A Δδ of 2.16 ppm for the trans form and ca. 1 ppm for the cis form of *N*,*N*-dimethylformamide was reported when α-naphthylamine was added as solvent to the pure liquid! Moriarty[33] reported a maximum upfield shift of 1.18 ppm for the trans isomer and 0.84 for the cis isomer of butyrolactam when diluted with benzene. Hence, the observed solvent shifts corroborate the assignments made on the basis of chemical shift arguments. These upfield shifts in aromatic solvents are attributed to *selective shielding* of the proton (or alkyl group) trans to the amide carbonyl group by the aromatic solvent. Preferential complexation of an aromatic solvent in the E_{anti} and Z_{anti} forms causes shielding of H-2 and H-4, respectively.



C. NMR Studies of Stereochemistry of Alkylated Reissert Compound 8. The solution ^1H NMR spectra of 8 at ambient temperature and 213 K showed only one signal in the methyl region in both $CDCl_3$ (Figure 3) and $C_6D_5CD_3$. Table V lists δ and Δδ values.

Perusal of Table V indicates that 8 exists in the *Z* form. A comparison of the H-4 shifts of 8 to H-4 shift values for the *Z* form of 2 in $CDCl_3$ (5.9, Table II) and in $C_6D_5CD_3$ (5.7, Table III) indicates comparable values but those for the *E* form of 2 are very different. ASIS value for H-4 of 8 are the same as for the *Z* form of 2 in Table IV, thus lending more support to the existence of the alkylation product in the *Z* form. If the *E* form has been present, then its H-4 signals would have been far downfield (at ca. 8 ppm) due to the influence of the C=O linkage, just as in 2 (Tables II and III). Signal doubling does not occur as the temperature is changed from ambient to 213 K (−60 °C). This means that *either* there is only one conformer present *or* that interconversion of the two rotamers is still occurring rapidly at 213 K. In fact, upon methylation we expect to increase the steric bulk around C-2 which in

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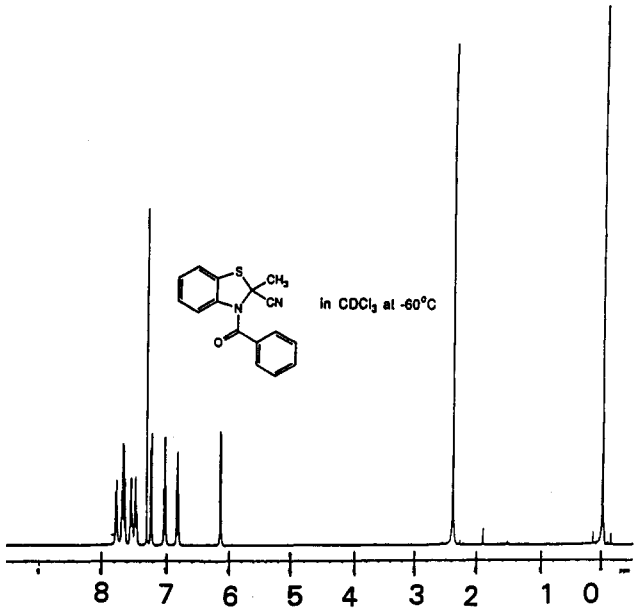
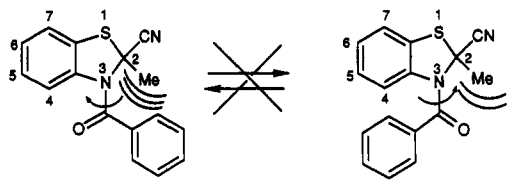


Figure 3. 400-MHz ^{1}H NMR spectrum of 8 in $CDCl_3$ at 213 °K.

Table V. ASIS Results for 8 at 294 and 213 K

	CH_3		H-4	
	294 K	213 K	294 K	213 K
δ ($CDCl_3$)	2.33	2.39	6.12	6.15
δ ($C_6D_5CD_3$)	1.95	1.84	5.87	5.80
$\Delta\delta$ (ppm)	+0.38	+0.55	+0.25	+0.35

turn would increase the interconversion barrier from the *Z* to the *E* form and raise the energy of the *E* isomer. Indeed molecular mechanics calculations[29] for the *E* and the *Z* forms of 8 indicate that the *Z* form is more stable than the *E* by >2.5 kcal/mol, leading to a *Z*/*E* ratio of >99:1 (298 K). As in the Reissert compounds, the aromatic ring of the aryl group is nearly orthogonal (ca. 70°) to the plane of the C=O linkage. Therefore, the introduction of the methyl group yields only one rotamer as shown below. This situation is analogous to findings in alkylated isoquinoline Reissert compounds.[25]



8E **8Z**

Experimental Section

All melting points are corrected. Tetramethylsilane was used as an internal standard for recording ^{1}H NMR spectra. FTIR spectra were recorded as KBr pellets. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Reissert Compounds. A general proceudre for 1 exemplifies those for 2–5.

2-Cyano-3-(*o*-chlorobenzoyl)-2,3-dihydrobenzothiazole (1). Benzothiazole (9.5 g, 66 mmol) was dissolved in 60 mL of CH_2Cl_2 under N_2, 9.0 mL (68 mmol) of *o*-chlorobenzoyl chloride was added, and the mixture was homogenized by magnetic stirring. A catalytic amount of $AlCl_3$ was then added along with 9.5 mL (69 mmol) of trimethylsilyl cyanide (TMSCN). The honey-colored solution gave a steady exotherm for about 20 min and within 1 h, a white solid started forming. The stirring had stopped in another hour and the heterogeneous mixture was allowed to stand for 8 h. The solvent and other volatiles were evaporated in vacuo to give a pale yellow solid (20.2 g, 100%), mp 179.5–181.5 °C. Recrystallization from 3:7 DMF/EtOH (100 mL) yielded shiny white crystals: mp 183.5–185.00 °C; FTIR (cm^{-1}) 1664 (carbonyl), 1464 (arom C=C), 750 (C–Cl) and 740 (o-disubstituted benzene); ^{1}H NMR ($CDCl_3$) δ 7.75–7.40 (m), 7.40–7.20 (m), 7.20–7.00 (br s), 6.95–6.65 (br s), 6.20–5.90 (br s).

2-Cyano-3-*o*-toluoyl-2,3-dihydrobenzothiazole (2): FTIR (cm^{-1}) 1662 (carbonyl), 1465 (arom C=C), 1325 (CH_3 attached to a phenyl ring), 737 (o-disubstituted benzene); ^{1}H NMR ($CDCl_3$) δ 7.8–7.4 (m), 7.4–7.2 (d, unresolved), 7.2–7.0 (br t), 7.0–5.5 (m), 2.9–1.8 (2 br m).

2-Cyano-3-benzoyl-2,3-dihydrobenzothiazole (3): ^{1}H NMR ($CDCl_3$) δ 7.65–7.55 (m, 3 H), 7.55–7.40 (m, 2 H), 7.31 (d, 1 H, J = 7.2 Hz), 7.09 (dd, 1 H, J = 7.5, 7.2 Hz), 6.98 (dd, 1 H, J = 7.5, 7.2 Hz), 6.89–6.68 (br, 1 H), 6.36 (s, 1 H).

2-Cyano-3-*p*-toluoyl-2,3-dihydrobenzothiazole(4): ^{1}HNMR ($CDCl_3$) δ 7.48 (d, 2 H, J = 7.0 Hz), 7.40–7.22 (m, 3 H), 7.15–6.95 (m, 2 H), 6.90–6.60 (br s, 1 H), 6.35 (s, 1 H), 2.45 (s, 3 H).

2-Cyano-3-(*p*-*tert*-butylbenzoyl)-2,3-dihydrobenzothiazole (5): FTIR (cm^{-1}) 2237 (v weak, CN), 1654 (carbonyl), 1464 (arom C=C), 1352, 1332 (*tert*-butyl); ^{1}H NMR ($CDCl_3$) δ 7.55 (d, 2 H, J = 8.4 Hz), 7.47 (d, 2 H, J = 8.4 Hz), 7.28 (d, 1 H, J = 8.2 Hz), 7.10 (dd, 1 H, J = 7.5, 7.7 Hz), 7.01 (dd, 1 H, J = 7.5, 7.4 Hz), 6.97–6.77 (br s, 1 H), 6.33 (s, 1 H), 1.38 (s, 9 H).

Alkylation of Reissert Compounds. A general procedure for 6 exemplifies those for 7–9 except the temperature for the synthesis of 9 was −23 °C.

2-Cyano-2-methyl-3-(*o*-chlorobenzoyl)-2,3-dihydrobenzothiazole (6). 2-Cyano-3-(*o*-chlorobenzoyl)-2,3-dihydrobenzothiazole (1, 1.91 g, 6.3 mmol) was dissolved with slight heating in 15 mL of DMF and after cooling to 0–5 °C, 2.4 mL (38 mmol) of MeI were added and the mixture was magnetically stirred until homogeneous. NaH (60% dispersion in mineral oil, 0.28 g, 7 mmol) was added quickly in one portion. A pale yellow color was evident after 10 min along with some formation of solid. DMF (3 mL) was added and stirring was continued for 3 h. The reaction was poured into 200 mL of ice-cold water. A pale yellow oil settled which was washed with water and hexanes and dried in vacuo to obtain 1.7 g (85%) of a gummy solid, trituration of which with EtOH yielded an off-white solid which was crystallized from 95% EtOH: mp 163.8–164.8 °C; FTIR (cm^{-1}) 2237 (v weak, CN), 1657 (carbonyl), 1471 (arom C=C), 1350 (CH_3 antisym def) and 741 (o-disubst benzene); ^{1}H NMR ($CDCl_3$) δ 7.65–7.34 (m, 4 H), 7.15 (d, 1 H, J = 7.9 Hz), 6.98 (dd, 1 H, J = 7.9, 6.4 Hz), 6.75 (dd, 1 H, J = 6.4, 7.0 Hz), 6.02 (d, 1 H, J = 7.0 Hz) and 2.60–2.15 (br s, 3 H).

2-Cyano-2-methyl-3-*o*-toluoyl-2,3-dihydrobenzothiazole (7): FTIR (cm^{-1}) 2236 (v weak, CN), 1659 (carbonyl), 1470 (arom C=C), 1320 (CH_3 attached to benzene ring), 737 (o-disubt benzene); ^{1}H NMR ($CDCl_3$) δ 7.40 (m, 2 H), 7.30 (m, 2 H), 7.15 (d, 1 H, J = 7.8 Hz), 6.95 (dd, 1 H, J = 7.8, 8.7 Hz), 6.70 (dd, 1 H, J = 8.7, J = 7.8 Hz), 5.90 (d, 1 H, J = 7.8 Hz), 2.45 (br s, 6 H).

2-Cyano-2-methyl-3-benzoyl-2,3-dihydrobenzothiazole (8): ^{1}H NMR ($CDCl_3$) δ 7.71–7.63 (m, 2 H), 7.63–7.52 (m, 1 H), 7.51–7.39 (m, 2 H), 7.18 (d, 1 H, J = 7.4 Hz), 6.96 (dd, 1 H, J = 6.8, 7.4 Hz), 6.78 (dd, 1 H, J = 7.9, 7.4 Hz), 6.13 (d, 1 H, J = 7.9 Hz), 2.33 (s, 3 H).

2-Cyano-2-(*p*-chlorobenzyl)-3-benzoyl-2,3-dihydrobenzothiazole (9): FTIR (cm^{-1}) 1655 (carbonyl), 1468 (arom C=C), 1319 (methylene rock), 748 (o-disubst benzene); ^{1}H NMR ($CDCl_3$) δ 7.72–6.70 (m, 12 H), 6.03 (d, 1 H), 3.95 (d, 1 H, J = 13.2 Hz), 3.72 (d, 1 H, J = 13.2 Hz).

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