MASS-SPECTROMETRIC STUDY OF SULFENAMIDE DERIVATIVES OF 2-SUBSTITUTED BENZOTHIAZOLES

Yu. G. Chikishev, N. A. Klyuev, and G. A. Vakhtberg

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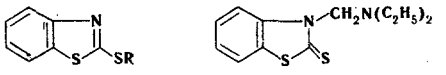
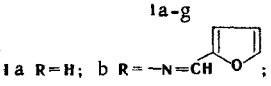
It is shown that the dissociative ionization of 2-mercaptobenzothiazole derivatives with a sulfenamide bond is accompanied by cleavage of the labile N–S bond and simultaneous migration of the hydrogen atom from the thiol substituent at the site of cleavage to the sulfur atom. Ion peaks with mass 167, 166, R, and (R–H), where R is an N-substituted cycloalkylamine, are maximum peaks and are used for the identification of the compounds.

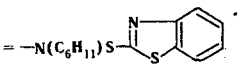
In order to make a qualitative and quantitative analysis of the volatile substances that are liberated from rubber and latex articles, we studied the mass spectra of individual derivatives of 2-substituted benzothiazoles (Ia-g, II). The compounds in this series are standard and widely used vulcanization accelerators.



Ia-g

II

Ia R=H; b R=  ; c R=—N(CH$_2$CH$_2$)$_2$O; d R=—NHC$_6$H$_{11}$;

e R=—N(CH$_2$)$_6$; f R=—N(C$_6$H$_{11}$)$_2$; g R=—N(C$_6$H$_{11}$)S 

The mass spectra of Ia-g and II were recorded by direct introduction of the substances into the ion source. The mass spectra of Ia-g and II are presented in Table 1; the stabilities of the compounds with respect to electron impact (W_M), their selectivities ($S_{1/2}$), and the total ion currents (ΣI) are also given in Table 1.

The mass spectrum of Ia is described in [1, 2]. However, one should note that the difference in the relative intensities for certain ion peaks (for example, those with m/e 140, 135, 108, 96, and 91) in the mass spectra obtained reaches 44% in individual cases. The mass spectra of Ic, d [3], which were not expressed in tabular form, were also partially presented, but the mechanism and peculiarities of the fragmentation of these compounds were not discussed. All of the above-indicated mass spectra of the compounds were obtained with a spectrometer with direct introduction of the sample into the ion source.

It follows from an analysis of the mass spectrum of I that the formation of the primary fragment ions a-g from ion M^+ is not realizable without its prior isomerization. It should be assumed that the M^+ ion exists in states A-D. The formation of the cyclic forms A and B of the M^+ ion is associated with a dynamic thiol–thione equilibrium [3]. The appearance in the spectrum of $(M-HCN)^+$ and $(M-NCS)^+$ ion peaks constitutes evidence for the presence of the corresponding open isomeric forms – C and D – for the M^+ ion, and the formation of the C form is accompanied by migration of a hydrogen atom from the thiol substituent.*

It follows from a comparison of the total intensities of the peaks of ions whose formation is associated with the primary acts of fragmentation of the M^+ ion that the contribution of thione form B to the total ion

*Here and subsequently, the numbers under the formulas indicate the mass number of the ion and the numbers with asterisks indicate the apparent mass of the metastable transition.

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TABLE 1. Mass Spectra of I and II (the peaks of ions with intensities ≥ 5% of the maximum ion peak in the spectrum are indicated)

Compound Ia. 32 (6.4), 45 (6,5), 63 (11,2), 64 (5,1), 69 (15,6), 82 (6,9), 83,5 (5,6), 91 (9,1), 96 (9.7), 103 (5.2), 108 (14.7), 109 (13,3), 122 (5,2), 123 (9,1), 135 (6.5), 140 (7,5), 166 (6.1), **167 (100,0)**, 168 (10.5), 169 (8,0); W_M=27,9; $S_{1/2}$=7,5; ΣI=357,1

Compound II. 45 (12,0), 48 (6.3), 50 (6.1), 51 (6.4), 58 (11,7), 63 (16,7), 64 (17,9), 65 (6.0), 69 (22.9), 70 (6.4), 82 (8.5), 83.5 (10.6), 86 (8.4), 91 (12.4), 96 (15.0), 100 (9.3), 103 (6.0), 108 (19,7), 109 (18.7), 122 (6,5), 123 (13,7), 135 (9,5), 140 (7,9), 151 (6,6), 166 (6.3), **167 (100.0)**, 168 (11,9), 169 (9,8), 252 (5,7), 253 (3,1). W_M=1,0; $S_{1/2}$=13,0; ΣI=598,5

Compound Ib. 45 (7.1), 108 (19.5), 109 (5.8), 122 (10.3), 123 (8.7), 166 (9,9), **167 (100,0)**, 168 (12.1), 169 (9,1), 260 (8.2), 261 (2,0), W_M=3,0; $S_{1/2}$=4,0; ΣI=275,2

Compound Ic. 41 (9,0), 43 (7.7), 44 (9,6), 45 (8,7), 54 (6,3), 55 (7,0), 56 (60,0), 57 (11,3), 58 (5,7), 60 (15.7), 63 (8,7), 69 (12,7), 82 (5,7), 86 (73,3), 90 (5,3), 102 (5,0), 108 (23,0), 122 (9,7), 134 (5,4), 135 (13,0), 162 (7,0), 163 (11,3), 166 (15,7), **167 (100,0)**, 168 (13,3), 169 (11,3), 220 (8,7), 252 (4,7); W_M=0,6; $S_{1/2}$=10,0; ΣI=738,5

Compound Id. 41 (40,0), 42 (9,5), 43 (25,0), 44 (11,5), 45 (6,0), 47 (17,7), 48 (10,0), 49 (5,5), 53 (5,5), 54 (16,4), 55 (40,4), 56 (38,0), 57 (11,0), 63 (7,3), 67 (5,9), 68 (5,4), 69 (19,3), 70 (7,6), 81 (10,0), 82 (7,4), 83 (43,6), 85 (29,5), 91 (6,3), 96 (8,3), 97 (9,5), **98 (100,0)**, 99 (15,2), 102 (5,7), 108 (28,1), 109 (10,3), 122 (10,8), 123 (7,4), 135 (13,5), 136 (7,1), 149 (16,6), 150 (14,1), 166 (22,8), 167 (78,0), 168 (28,1), 169 (13,5), 181 (7,3), 182 (24,9), 221 (12,4), 264 (9,8), 265 (7,0); W_M=1,0; $S_{1/2}$=12,0; ΣI=952,3

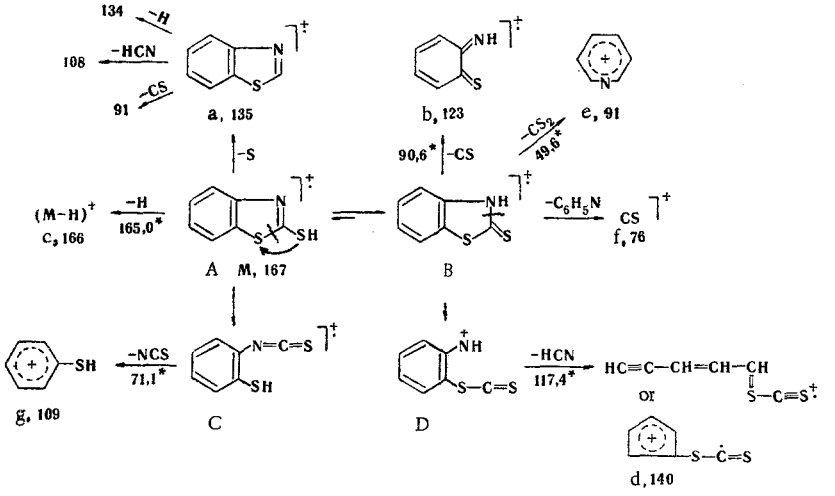
Compound Ie. 39 (8,7), 41 (21,7), 42 (15,2), 43 (13,0), 44 (13,0), 55 (12,0), 56 (10,9), 57 (8,7), 68 (6,5), 69 (10,9), 70 (10,9), 82 (5,4), 97 (6,5), **98 (100,0)**, 99 (15,2), 108 (8,7), 109 (5,4), 135 (8,7), 149 (5,4), 150 (6,5), 166 (7,6), 167 (67,4), 168 (9,8), 169 (6,5), 232 (5,3), 264 (2,2), W_M=0,4; $S_{1/2}$=8,5; ΣI=518.5

Compound If. 39 (13,0), 41 (49,3), 43 (10,8), 44 (12,3), 53 (6,5), 54 (12,2), 55 (71,3), 56 (24,6), 67 (7,7), 68 (6,8), 69 (15,8), 79 (5,5), 81 (12,3), 82 (13,9), 83 (24,3), 96 (14.4), 97 (7,9), **98 (100,0)**, 99 (8,1), 108 (13,0), 123 (5,4), 124 (5,3), 136 (34,6), 137 (8,5), 138 (17,3), 150 (5,9), 151 (6,0), 166 (14,3), 167 (44,4), 168 (17,0), 169 (5,0), 179 (19,5), 180 (93,6), 181 (23,3), 346 (0,5); W_M=0,03; $S_{1/2}$=7,5; ΣI=835,1

Compound Ig. 39 (10,3), 41 (13,4), 43 (9.4), 44 (5,6), 54 (6,4), 55 (33,1), 56 (15,7), 69 (8,2), 83 (8,1), 91 (6,3), 95 (6,8), 96 (19,4), 98 (93,6), 99 (8,0), 108 (21,5), 109 (14,2), 122 (9,1), 123 (11,1), 127 (9,4), 135 (5,5), 149 (8,5), 150 (6,7), 166 (25,8), **167 (100,0)**, 168 (21.5), 169 (13,1), 182 (11,7), 219 (12,8), 220 (9,6), 221 (5,7), 229 (14,7), 262 (12,3), 264 (7,0); W_M=0; $S_{1/2}$=12,5; ΣI=781,2

current is greater by a factor of almost two than the contribution of thiol structure A. This relationship is also retained as the ionizing-electron energy is reduced to 15 eV. A shift in the equilibrium to favor the thione form is observed for Ia, according to the UV spectroscopic data [4].

In [1], Millard and Temple associate the formation of the $(M-H)^+$ ion with randomized loss of hydrogen from the benzene fragment of the molecule; however, this can scarcely occur. It was shown in [5] that the elimination of hydrogen from the benzothiazole molecule is realized exclusively from the 2 position. In addition, in the case of randomized loss, the ratios of the intensities of the ion peaks (I_{135}/I_{134} and I_{167}/I_{166}) in the benzothiazole and Ia molecules should be approximately identical [6, 7].

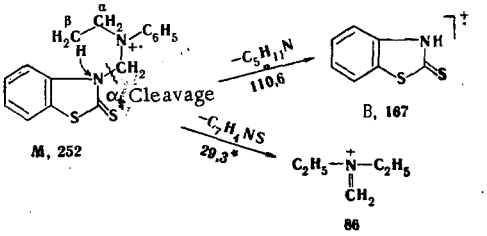


This was not observed, from which it followed that the elimination of hydrogen from the M^+ ion is realized from the thiol substituent (form A).

TABLE 2. Fragment Peaks of Ions Used for the Identification of Ia-g and II (the peak intensities are expressed in percent of the total ion current)

Ions	Compounds							
	Ia	II	Ib	Ic	Id	Ie	If	Ig
$(M-S)^+$	1,8	—	—	1,2	—	1,0	—	—
R^+	—	—	1,3	9,9	10,5	19,3	12,0	0,5
$(R-H)^+$	—	—	1,0	0,6	1,0	1,3	2,5	1,6
A+(B,C,D) (*m/e* 167)	27,9	16,7	36,4	13,5	8,2	13,0	5,7	12,8
a (*m/e* 135)	1,8	1,6	1,0	1,8	1,4	1,7	—	—
b (*m/e* 123)	2,5	1,3	3,2	—	0,8	—	—	1,4
c (*m/e* 166)	1,4	1,0	3,6	2,1	2,4	1,5	1,8	3,3
d (*m/e* 140)	2,1	1,3	—	—	—	—	—	—
e (*m/e* 91)	2,5	2,1	1,3	—	—	—	—	—
f (*m/e* 76)	0,6	—	—	0,5	—	—	—	—
g (*m/e* 109)	3,7	3,1	2,1	—	1,1	1,0	—	1,8
h (*m/e* 163)	—	—	—	1,5	—	—	—	—
i (*m/e* 150)	—	—	—	—	1,0	1,3	—	0,9
j (*m/e* 221)	—	—	—	—	1,3	—	0,6	0,8
k (*m/e* 182)	—	—	—	—	2,6	—	—	1,5
A+(B, C, D)/C	19,9	16,7	10,1	6,4	3,5	8,7	3,2	3,8

The appearance in the spectrum of II (Table 1) of fragment ions a-g and other ions (with masses 167, 166, 140, 135, 123, 122, 109, 108, 103, 96, 91, 82, and 69) constitutes evidence that the fragmentation of II is realized through a rearrangement process, which leads to the formation of a pseudomolecular ion with the 2-mercaptobenzothiazole structure, the peak of which is a maximum in the spectrum. The subsequent fragmentation of this ion serves as the reason for the appearance in the spectrum of fragments with the indicated mass numbers. Charge localization in the M^+ ion of II evidently occurs exclusively on the nitrogen atom in the aminoalkyl substituents, and in this case the cleavage that is characteristic for aliphatic amines [8, 9] is realized; this is indicated by the presence in the spectrum of a fragment ion with m/e 86 and the corresponding metastable transition. The α cleavage is accompanied by migration of a hydrogen atom to the nitrogen atom in the heteroaromatic ring. It is likely that this process is realized through a five-membered transition state in which the β-carbon atom is a hydrogen donor [3, 9, 10]. Ion B with m/e 167 is formed as a result of this sort of rearrangement.



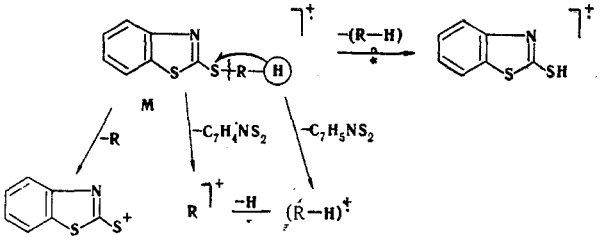
The presence of a labile sulfenamide bond in Ib-g predetermines its cleavage on electron impact (β cleavage relative to the thiazole ring of the molecule). Charge localization in the M^+ ion of Ib-g in both the benzothiazole portion and in substituent R promotes the appearance and formation of both molecular fragments in mass spectra. By analyzing the mass spectra of Ib-g (Table 1) one can arrive at the conclusion that, in addition to simple cleavage of the S–N bond, which proceeds to a smaller extent, cleavage associated with migration of a hydrogen atom from substituent R is also realized. As a result of this sort of rearrangement, the spectra of Ib-g always contain a pseudomolecular peak of an ion with structure A and the corresponding daughter peaks of fragment ions d-g. The peak of this ion, with mass 167, is, as a rule, a maximum peak in the spectra, and its intensity increases sharply as the ionizing-electron energy decreases (by a factor of almost two to four at 15 eV), while the intensity of the ion peaks due to the usual β cleavage remain within their earlier limits.

Thus the general trend of the fragmentation of Ib-g constitutes evidence that the identification and qualitative analysis of substances of this type should be made on the basis of a detailed examination of the fragmentation processes of ions with structures R^+ and $(R-H)^+$, especially since the W_M values of such structures range from 0 to 1% of the total ion current, and this does not make it possible to use the M^+ ion peak as an analytical peak.

The fragmentation of compounds with structures analogous to R^+ and $(R-H)^+$ was studied in detail in [11-13] for a number of furan derivatives, cyclohexylamines, hexamethyleneimine, and morpholine, and the interpretation of the fragment ions determined by the structure of substituent R does not raise any difficulties.

The elimination and migration of a hydrogen atom in samples of Ic-g, in which substituent R is a cycloalkylamine or a cyclic amine, will always be realized from the most highly substituted α-carbon atom (relative to the nitrogen atom) [12, 13].

Thus the overall pattern of the fragmentation of Ib-g under the influence of electron impact can be described by the following scheme:

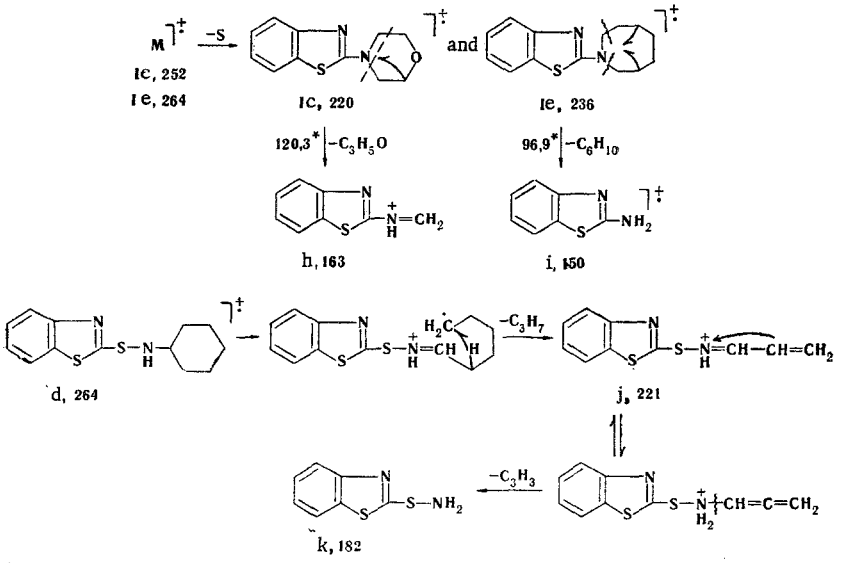


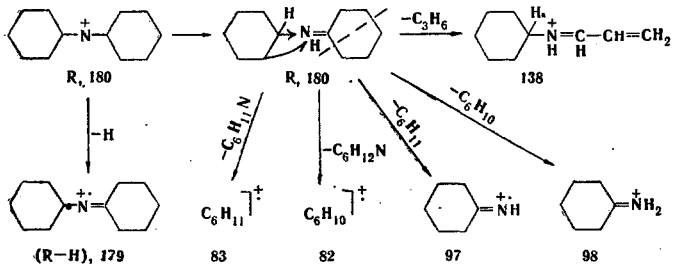
In addition to the fragment ions obtained as a result of fragmentation of the Ib-g molecules, several specific fragmentation processes that it is desirable to use for identification purposes (Table 2) are characteristic for this series of compounds. For example, ejection of a sulfur atom from the M^+ ion (which, in principle, is uncharacteristic for cycloalkyl aryl sulfides [14]) is realized for samples of Ic and Ie, and the process is fixed by the corresponding metastable transition. The pseudomolecular $(M-S)^+$ ion has a 2-morpholinobenzothiazole structure (for Ic) and a 2-hexamethyleneiminobenzothiazole structure (for Ie); the intensity of the peak of this ion increases appreciably (~4.5 times) as the ionizing-electron energy is reduced to 15 eV. The subsequent fragmentation of this ion proceeds through destruction of the ring of R, which is accompanied by migration of a hydrogen atom to the nitrogen atom. The β-carbon atom of the ring is evidently a hydrogen donor [12, 13, 15]. The fragmentation of ions with structures h and i was described in [1, 2, 16].

Fragmentation of the cycloalkyl grouping is also observed for Id. Successive elimination of alkyl fragments from the M^+ ion leads to the formation of ions j and e and the interpretation of the subsequent fragmentation of the latter was accomplished in [2, 16].

One should have expected the formation of ions of this type in the mass spectra of If and Ig (Table 1). However, this process is characteristic only for Ig and is observed after the step involving the formation of ions with m/e 264 and 263 due to cleavage of the N–S bond and subsequent elimination of a radical and a 2-mercaptobenzothiazole molecule from the M^+ ion, which is determined from the presence of j and k ion peaks in the spectrum of Ig.

The formation of an ion peak with m/e 180 with a dicyclohexylamine cation structure in the mass spectrum of If is due to the structure of substituent R. The axially oriented hydrogen atoms in the cyclohexyl radicals cause certain steric hindrances, which can be eliminated only by cleavage of the labile N–S bond in the M^+ ion or by detachment of one of them. The latter should have led to the known mass spectrum of Id or Ig.





However, we did not observe this process. The fragmentation of the dicyclohexylamine cation is realized as in the case of ordinary amines.

The structure of the ion with m/e 138 is indirectly confirmed by the high-resolution mass spectrum. The calculated mass (138, 1298) for empirical formula $C_9H_{16}N$ is in good agreement with the experimentally found value (138, 1288).

It follows from Tables 1 and 2 that the maximum ion peaks in the mass spectra of Ia-g correspond, as a rule, to A^+ (B, C, D) and R^+ fragments, i.e., to those ions whose formation is due to cleavage of the labile sulfenamide bond. It is known [2, 17, 18] that a correlation between the thermal cleavage of the bond and the cleavage of the same bond under the influence of electron impact is possible; on the other hand, the thermal effect exerted on Ia-g and II during vulcanization is also associated with homolytic cleavage of the N—S bond [19].

The presence of amine and benzothiazole cations corresponds to opening of the S_8 ring during vulcanization [20]. In this case, the benzothiazole cation should be readily reduced to an anion during reductive vulcanization. It is then completely likely that the activity of the accelerator can be characterized, on the one hand, by the magnitude of the ratio of the A^+ (B, C, D)/c^+ ion peaks (i.e., m/e 167 : m/e 166), and, on the other hand, by the intensity of the ion peak of amine radical R^+, which constitutes evidence for the ease of formation of the amine (Table 2).

EXPERIMENTAL

The mass spectra of Ia-g and II (purity ≥ 98.5%) were recorded with a Varian MAT-311 spectrometer with direct introduction of the samples into the ion source. The conditions under which the spectra were recorded were as follows: The ionizing voltages were 70 and 20 eV, the cathode emission currents were 100 and 50 μA, respectively, the accelerating voltage was 3 kV, and the source temperature was 180-200°. The reproducibility of the spectra was 2-3 rel. % in both cases.

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CONFIGURATION OF 2-SUBSTITUTED 1-AMINOETHYLENEIMINES

S. A. Giller,* É. É. Liepin'sh,
A. V. Eremeev, I. Ya. Kalvin'sh,
V. A. Kholodnikov, and V. A. Pestunovich

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The trans configuration of 2-phenyl- and 2-methyl-1-aminoethyleneimine was proved by means of their PMR spectra in the presence of tris(dipivaloylmethanato)europium.

The establishment of the configurations of 2-substituted 1-aminoethyleneimines directly from the chemical shifts of the protons of the three-membered ring in the PMR spectra requires prior knowledge of the effect in these compounds of the anisotropy of the adjacent groups, the magnitude of which can currently be evaluated only extremely approximately. In order to establish the spatial orientation of the amino group, we used tris(dipivaloylmethanato)europium [$Eu(DPM)_3$], inasmuch as one may expect that complexing will occur only at one nitrogen atom at low concentrations of this paramagnetic-shift reagent. This assumption is confirmed experimentally: Up to $C_{Eu(DPM)_3}/C_{substance} \leq 0.3$-0.4, deviation from the linear dependence of the chemical shift (τ) on $C_{Eu(DPM)_3}/C_{substance}$ is not observed.

The results obtained after mathematical treatment of the linear dependences of the $\tau = A - BD$ type, where $D = C_{Eu(DPM)_3}/C_{I\text{-}III}$, are presented in Table 1.

*Deceased.

TABLE 1. Coefficients of the Calculated Linear Dependences and Their Mean-Square Error and Correlation Coefficients

Compound	τ*	A	B	r	s
1-Aminoethyleneimine (I)	H_{cis}	8,56	52,87	0,99	0,36
	H_{trans}	8,12	50,94	0,99	0,29
	H_2	5,71	91,52	0,99	0,57
2-Phenyl-1-aminoethyleneimine (II)	H_2	7,70	21,38	0,99	0,18
	†$H_{3\,cis}$	8,52	16,73	0,99	0,17
	H_{trans}	8,35	21,58	0,99	0,17
2-Methyl-1-aminoethyleneimine (III)	H_2	8,48	51,60	0,99	0,12
	†$H_{3\,cis}$	8,47	16,71	0,99	0,03
	$H_{3\,trans}$	8,65	35,30	0,99	0,02
	CH_3	8,88	21,29	0,99	0,06

*$\tau = A - B\,[C_{Eu(DPM)_3}/C_{I\text{-}III}]$.
†With respect to the substituent in the 2 position.

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