ISOPROPYL *N*-ARYLMALONAMATES. SYNTHESIS, STRUCTURE, CONFORMATION AND REACTIONS WITH CARBON DISULFIDE

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Dedicated to the memory of Professor Alexander Perjéssy.

Acylation of aromatic amines **1** with diisopropyl malonate (**2**) leads to a mixture of isopropyl *N*-arylmalonamates **3** and malonanilides **4**. The reaction of **3** with carbon disulfide in the presence of sodium hydride gives disodium salts **5**. Treatment of **5** with an alkylating agent yields the open-chain or cyclic ketene dithioacetals **6**, **7** or **8**. The molecular structure, hydrogen bonding and preferential conformation of the isopropyl *N*-arylmalonamates **3**, **6** and **7** were investigated using correlation analyses of IR, ^{13}C NMR and AM1 semiempirical data.

Keywords: Malonates; *N*-Arylmalonamates; Ketene dithioacetals; AM1 calculations; Correlation analysis; Conformational analysis.

Alkyl *N*-arylmalonamates are valuable building blocks in the synthesis of numerous aromatic and heterocyclic compounds with a wide spectrum of biological activity[1–5]. On the other hand, ketene dithioacetals bearing electron-withdrawing groups are useful and versatile reagents for the synthesis of heterocycles[6–9]. In general, ketene dithioacetals are obtained by the reaction of active methylene compounds with carbon disulfide in the presence of a base followed by alkylation[10].

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In our investigations of the preparative use of push-pull alkenes, the reactions of carbon disulfide with isopropyl *N*-arylmalonamates are to be proved. From the viewpoint of the conformation and inter- and intramolecular interactions, isopropyl *N*-arylmalonamates are an interesting group of compounds, which deserve more particular structural investigations using spectral and theoretical methods. For this purpose, a part of this study was aimed at IR, ^{13}C NMR and AM1 semiempirical investigations to find preferential structural properties of compounds in the series **3**, **6** and **7**.

RESULTS AND DISCUSSION

Alkyl *N*-arylmalonamates can be prepared by reaction of arylamines with various malonic acid derivatives, such as chlorides[11] or anhydrides of monoalkyl esters[1,11], but most frequently dialkyl malonates are used[11–13]. We have found that acylation of aromatic amines **1** with diisopropyl malonate (**2**), both in equimolar ratio and in an excess of the latter, at 170 °C is practically always accompanied by an undesired side-reaction, the formation of dianilides **4**. This fact is in accordance with results that malondianilides can be synthesized in high yields by heating ethyl *N*-arylmalonamates to 170–220 °C without any solvent irrespective of substituents in the aromatic ring[11] (Scheme 1).

Reactions of CH-acid compounds such as malononitrile, ethyl cyanoacetate, cyanoacetamide or malonic esters with carbon disulfide were studied intensively[9]. Whereas malononitrile and ethyl cyanoacetate treated with carbon disulfide provide high yields, malonic esters and cyanoacetamide give only moderate yields of the corresponding dithioacetals.

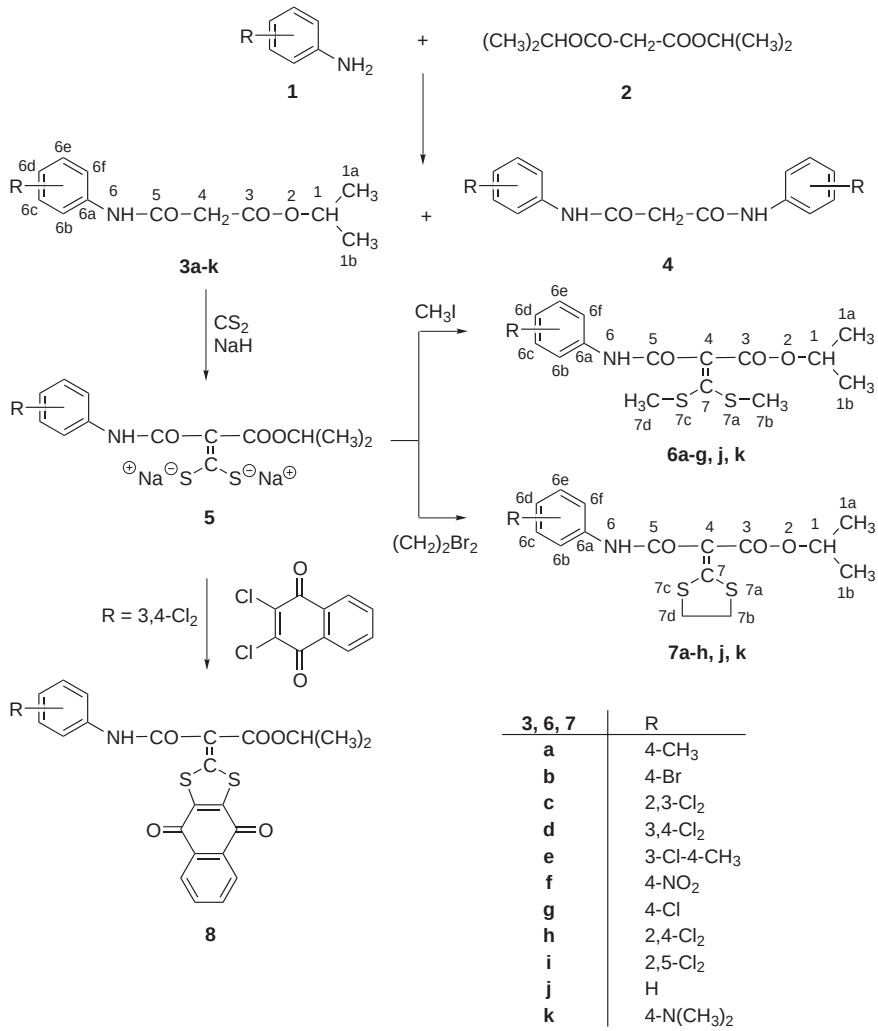
Isopropyl *N*-arylmalonamates **3** were treated with carbon disulfide in dimethyl sulfoxide in the presence of sodium hydride to give geminal dithiolates **5** which were not isolated. Using alcoholic potassium hydroxide, sodium ethylate or sodium *tert*-pentylate as bases, dithiolates were formed only in small amounts. Treatment of disodium salts **5** with two equivalents of methyl iodide led to isopropyl *N*-aryl-2-[bis(methylsulfanyl)-methylidene]malonamates **6** in a one-pot reaction. Using 1,2-dibromoethane for the alkylation of **5**, isopropyl *N*-aryl-2-(1,3-dithiolan-2-ylidene)-malonamates **7** were obtained. Using 2,3-dichloro-1,4-naphthoquinone gave condensed dithiol **8**.

The IR spectra of the open-chain as well as the cyclic ketene dithioacetals **6** and **7** show the C=C stretching vibration in the region 1578–1610 cm^{-1}. The ester band is shifted to lower wavenumbers (1674–1693 cm^{-1}). The band of the anilide group is found at 1630–1683 cm^{-1}. The selected IR spec-

tral data, namely the wavenumbers $\nu(C^3{=}O)$, $\nu(C^5{=}O)$ and $\nu(C^4{=}C^7)$ are listed in Table I.

^{1}H NMR spectra of compounds **6** and **7** show singlets at δ 2.44–2.49 and 3.30–3.37 ppm, respectively, corresponding to the SCH_3 and $S–CH_2–CH_2–S$ groups.

The synthesized isopropyl malonamates **3**, **6** and **7** are conformationally flexible compounds which can be fixed by hindered rotation and inter- or intramolecular hydrogen bonds. Possible structural forms of these com-



3, 6, 7	R
a	4-CH_3
b	4-Br
c	2,3-Cl_2
d	3,4-Cl_2
e	3-Cl-4-CH_3
f	4-NO_2
g	4-Cl
h	2,4-Cl_2
i	2,5-Cl_2
j	H
k	4-$N(CH_3)_2$

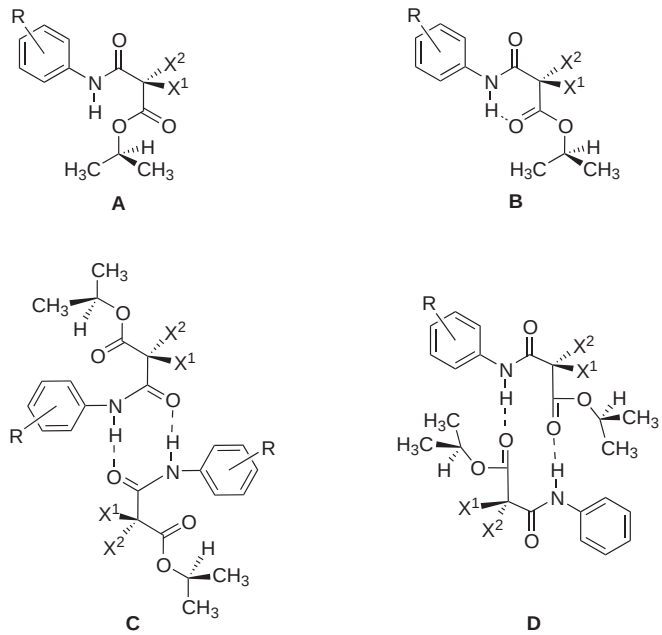
SCHEME 1

TABLE I
IR spectral data of isopropyl malonamates **3**, **6** and **7** in chloroform[a]

Compound	$\tilde{\nu}$, cm^{-1}		
	$\nu(C^3=O)$	$\nu(C^5=O)$	$\nu(C^4=C^7)$
3b	1718.4	1686.4	–
3c	1718.4	1692.8	–
3d	1718.4	1691.0	–
3e	1718.0	1686.4	–
3f	1718.4	1697.0	–
3g	1717.5	1686.4	–
3h	1718.4	1682.8	–
3i	1718.4	1692.8	–
3j	1718.4	1680.1	–
3k	1715.2	1674.0	–
6a	1692.8	1672.0	1596.8
6b	1692.8	1678.0	1590.4
6c	1692.8	1680.0	1584.0
6d	1692.8	1680.0	1584.0
6e	1692.8	1676.0	1587.2
6f	1692.8	1683.0	1600.0
6j	1692.8	1675.0	1599.2
6k	1692.8	1668.0	1591.6
7a	1676.8	1631.0	1593.6
7b	1680.0	1634.0	1587.2
7c	1680.0	1638.4	1610.0
7d	1676.8	1638.4	1580.8
7e	1676.8	1633.0	1584.0
7f	1679.0	1641.0	1590.3
7g	1676.8	1635.0	1590.4
7h	1676.8	1638.0	1577.6
7j	1676.4	1632.0	1595.6
7k	1674.0	1630.0	1590.4

[a] For numbering atoms see Scheme 1.

pounds drawn on the basis of AM1 calculations are illustrated in Scheme 2. The aim of the present study was to find preferential structural forms for the individual series of compounds. For this purpose the IR and NMR spectral characteristics, as well as the AM1 theoretical data of compounds **3**, **6** and **7** were particularly investigated.



SCHEME 2

Table II shows the influence of the solvent and concentration on the IR spectral data of 4-bromo derivatives **3b**, **6b** and **7b**. In the case of compound **3b** the intensity of the ester C^3=O band is higher than that of the amide C^5=O band. The intensity ratio of these two bands does not substantially change on changing concentration. On the other hand, for compound **7b** the intensity of the ester C^3=O band is much lower than that of the amide C^5=O band. A comparison of the intensity ratios (η) shows that the intensity of the ester C^3=O band increases with regard to the intensity of the amide C^5=O band as the concentration of a solution of compound **7b** decreases. In the case of compound **7b** an additional absorption band appears in the region 1645–1640 cm^{-1}, which can be assigned to the intermolecularly hydrogen bonded ester carbonyl group, $\nu(C^3{=}O)_b$. The above described spectroscopic behavior well corresponds to the idea that in solutions of compounds **3** a conformation is preferred which is stabilized

TABLE II

Influence of the solvent and concentration on the IR spectral data of carbonyl groups[a] in isopropyl malonamates **3b**, **6b** and **7b**

Compd	$\tilde{\nu}$, cm^{-1}							Intensity ratio[d], CCl_4			
	$\nu(C^3{=}O)$		$\Delta\nu$[b]	$\nu(C^5{=}O)$		$\Delta\nu$[b]	$\nu(C^3{=}O)_b$[c]				
	CCl_4	$CHCl_3$		CCl_4	$CHCl_3$		CCl_4	$\eta(c_1)$	$\eta(c_2)$	$\eta(c_1)_b$	$\eta(c_2)_b$
3b	1720.8	1718.4	2.4	1695.6	1686.4	9.2	–	0.59	0.54	–	–
6b	1713.0	1692.8	20.2	1692.8	1678.0	14.8	–	1.36	1.11	–	–
7b	1721.6	1680.0	41.6	1682.4	1634.0	48.4	1640.8	3.75	3.63	1.02	0.97

[a] For numbering atoms, see Scheme 1. [b] Difference between the ν(C=O) values in CCl_4 and $CHCl_3$ (the solvent effect). [c] Absorption band corresponding to the ester C=O group bonded by intramolecular hydrogen bond (see Scheme 2). [d] $\eta(c)$, intensity ratio of the $\nu(C^5{=}O)$ and $\nu(C^3{=}O)$ absorption bands in CCl_4 at given concentrations (c) and cell pathlengths (d): $c_1 = 1 \times 10^{-2}$ mol/l (d_1 = 1 mm), $c_2 = 8 \times 10^{-3}$ mol/l (d_2 = 5 mm); $\eta(c_1)_b$, intensity ratio of the $\nu(C^3{=}O)_b$ and $\nu(C^3{=}O)$ absorption bands in CCl_4 at given concentrations (c_1, c_2) and cell pathlengths (d_1, d_2).

by intermolecular hydrogen bonding in which the amide carbonyl group C^5=O participates as hydrogen acceptor (form **C**, Scheme 2). The Δν values in Table II show that the influence of the solvent on the hydrogen-bonded amide C^5=O group is much stronger than on the free ester C^3=O group. The IR spectroscopic properties of compounds **3** are very close to those observed in the case of substituted acetanilides[14], which form intermolecularly hydrogen-bonded cyclic dimers. On the other hand, compounds **7** preferentially exist in monomeric form with an intramolecular hydrogen bond (form **B**). It is evident from Table II that for compounds **7** the difference between the solvent effects on both carbonyl groups is less pronounced being consistent with the intramolecularly hydrogen-bonded structure **B**. Finally, compound **6b** exhibits both in $CHCl_3$ and CCl_4 a considerable change in the position of the ester ν(C^3=O) values compared with the ester ν(C^3=O) values of compounds **3b** and **7b**. This indicates that compounds **6** probably exist in the form of intermolecularly hydrogen-bonded cyclic dimers in which the ester carbonyl group C^3=O is involved in the hydrogen-bonded structure (form **D**).

The ^{13}C NMR chemical shifts measured in $CDCl_3$ for the series of isopropyl malonamates **3**, **6** and **7** are given in Tables III–V.

TABLE III
^{13}C NMR chemical shifts $\delta(^{13}C_n)^a$ for series of compounds **3** in $CDCl_3$

Carbon[b]	Compound									
	3b	**3c**	**3d**	**3e**[c]	**3f**	**3g**	**3h**	**3i**	**3j**	**3k**[d]
1	69.97	70.00	70.18	69.88	70.41	70.01	70.07	70.11	69.82	69.61
3	169.34	169.09	169.45	169.36	169.40	169.46	169.17	169.11	169.44	169.59
4	41.75	42.05	41.52	41.84	41.58	41.68	41.87	41.90	41.90	41.81
5	163.36	163.46	163.40	163.34	163.77	163.29	163.35	163.38	163.20	162.79
1a	21.68	21.73	21.68	21.67	21.68	21.70	21.75	21.70	21.68	21.71
1b	21.68	21.73	21.68	21.67	21.68	21.70	21.75	21.70	21.68	21.71
6a	136.62	136.28	136.99	136.32	143.70	136.14	133.43	135.41	137.54	128.60
6b	121.63	122.03	121.71	120.67	119.50	121.32	122.49	121.31	120.11	121.87
6c	131.92	132.86	132.74	134.38	125.06	129.01	128.86	129.77	128.99	113.15
6d	117.09	125.51	127.65	132.03	143.35	129.47	129.27	124.74	124.50	147.98
6e	131.92	127.61	130.48	130.93	125.06	129.01	127.72	133.32	128.99	113.15
6f	121.64	119.81	119.26	118.37	119.50	121.32	122.49	121.58	120.11	121.87

[a] In ppm. [b] For numbering atoms, see Scheme 1. [c] $\delta(^{13}C)$ 19.45 ppm for CH_3 group of R. [d] $\delta(^{13}C)$ 41.01 ppm for CH_3 group of R.

The differential nuclear Overhauser effect (DIFNOE) experiments showed in the ^{1}H NMR spectra of compound **3e** that for isopropyl group the protons on C^{1a} and C^{1b} atoms are situated in the close proximity of the benzene ring protons attached to C^{6b} and C^{6f} atoms (i.e. in *ortho*-position). On the contrary, the DIFNOE experiments exhibited negative results for signals of isopropyl protons of compounds **6e** and **7e**. This can be regarded as further evidence that compounds **6** and **7** occurred preferably in the **B** form and that in the case of compounds **3** the existence of conformation **C** is more probable than the conformation where the isopropyl groups are remote from the protons in the *ortho*-position of the benzene ring.

To confirm the conclusions obtained from the results of IR and NMR experiments the AM1 theoretical data were calculated for the series of isopropyl malonamates **3**, **6** and **7**. The heats of formation (ΔH_f) calculated for

TABLE IV
^{13}C NMR chemical shifts $\delta(^{13}C_n)^a$ for series of compounds **6** in $CDCl_3$

Carbon[b]	Compound							
	6a[c]	**6b**	**6c**	**6d**	**6e**[d]	**6f**	**6j**	**6k**[e]
1	69.74	69.98	70.05	70.12	69.90	70.11	69.69	69.60
3	165.00	165.22	164.86	165.25	165.08	165.36	165.00	165.02
4	130.39	129.55	129.49	128.93	129.73	128.21	130.16	130.77
5	161.62	161.57	161.74	161.70	161.65	161.92	161.70	161.52
7	156.08	157.46	158.31	158.55	157.17	160.25	156.54	155.20
1a	21.68	21.62	21.64	21.66	21.67	21.66	21.62	21.69
1b	21.68	21.62	21.64	21.66	21.67	21.66	21.67	21.69
6a	135.50	136.70	136.30	137.24	136.49	143.72	137.68	127.53
6b	119.99	121.42	121.73	121.52	120.40	119.22	119.93	121.72
6c	129.51	131.99	132.76	132.82	134.50	125.11	130.16	113.05
6d	134.17	117.08	125.39	129.59	132.05	143.61	124.48	148.17
6e	129.57	131.99	127.75	130.49	130.98	128.11	130.16	113.05
6f	119.99	121.42	119.65	119.09	118.17	119.26	119.93	121.72
7b	18.31	18.48	18.50	18.57	18.47	18.70	18.39	18.19
7d	18.31	18.48	18.50	18.57	18.47	18.70	18.39	18.58

[a] In ppm. [b] For numbering atoms, see Scheme 1. [c] $\delta(^{13}C)$ 20.80 ppm for CH_3 group of R. [d] $\delta(^{13}C)$ 19.40 ppm for CH_3 group of R. [e] $\delta(^{13}C)$ 40.92 ppm for CH_3 group of R.

forms **A**–**D** resulting from hindered rotation and hydrogen-bonding interactions are given in Table VI. The C^5=O bond orders and C^5 and H^6 charge densities are listed in Table VII. It is evident from Table VI that for compounds **3** the most stable form is **C**, where two molecules are intermolecularly hydrogen-bonded forming a cyclic dimer with the participation of the amide C=O groups. This is similar to acetanilide **9** (ref.[14]) and is in good agreement with the previous evidence based on the IR and NMR spectral results. On the other hand, in compounds **7** the form **B** has the lowest energy and the calculated distance between the hydrogen atom of the N–H group and the oxygen atom of the ester C^3=O group is only 2.03 Å, which is adventageous for the formation of an intramolecular hydrogen bridge.

TABLE V
^{13}C NMR chemical shifts $\delta(^{13}C_n)^a$ for series of compounds **7** in $CDCl_3$

Carbon[b]	Compound							
	7b	**7d**	**7e**	**7f**	**7g**	**7h**	**7j**	**7k**[c]
1	70.69	70.79	70.61	71.10	70.63	70.61	70.46	70.26
3	165.72	165.74	165.72	165.94	165.70	165.45	165.67	165.64
4	110.14	109.59	110.14	109.49	110.03	110.21	110.51	110.79
5	163.06	163.14	163.06	163.53	163.11	163.22	163.13	162.73
7	181.13	182.87	181.93	184.20	182.12	182.87	181.57	180.24
1a	22.10	22.02	22.09	22.10	22.06	22.07	22.11	22.09
1b	22.10	22.02	22.09	22.10	22.06	22.07	22.11	22.09
6a	137.58	138.04	134.49	143.05	137.06	133.49	138.43	128.67
6b	121.75	121.17	124.09	119.40	121.36	124.09	120.87	121.80
6c	131.77	132.45	128.71	125.07	128.78	128.71	128.87	113.20
6d	116.20	126.40	128.37	144.59	128.51	128.37	123.82	147.59
6e	131.77	130.70	127.43	125.07	128.78	127.43	128.87	113.30
6f	131.75	119.04	122.75	119.40	121.36	122.75	120.87	121.80
7b	38.39	38.37	38.36	38.52	38.35	38.34	38.35	38.28
7d	37.19	37.16	37.17	37.30	37.15	37.21	37.16	37.11

[a] In ppm. [b] For numbering atoms, see Scheme 1. [c] $\delta(^{13}C)$ 41.01 ppm for CH_3 group of R.

Finally, the IR and NMR experimental data were correlated with Hammett σ constants[15] (Table VIII) and AM1 bond orders and charge densities (Table IX). In all cases only the spectral and theoretical characteristics of the amide C^5=O and N^6–H groups were considered since the data for other structural fragments did not change markedly with structural changes and their correlations provided statistically insignificant results. In a few cases some *ortho*-substituted derivatives were excluded from correlations because significant errors resulted from approximation of substituent constants for *ortho*-substitution by σ_p Hammett values. A comparison of the correlations of $\nu(C^5{=}O)$ and $\delta(H^6)$ values with Hammett σ constants (Table VIII) shows that the ρ values for series **3** are higher than those obtained for series **7**. This can be reasonably explained by an increase in the efficiency of transmission of substituent effects in the intermolecularly hydrogen-bonded cyclic dimers **C**, which is in a good agreement with earlier results reported for a series of 3-arylmethylenephthalimidines[16]. It follows from

TABLE VI
Heats of formation for different forms[a] of compounds **3j**, **6j** and **7j** (R = H) and acetanilide (**9**)

Compound	Form	$-\Delta H_f$ kJ/mol	$\Delta(\Delta H_f)$[b] kJ/mol	Preferential form
3j	**A**	437.7	–	**C**
	B	455.3	17.6	
	C[c]	457.5	19.8	
	D[c]	430.8	–6.9	
6j	**A**	331.0	–	**D**
	B	344.0	13.0	
	C[c]	310.2	20.8	
	D[c]	351.2	20.2	
7j	**A**	310.8	–	**B**
	B	314.2	3.4	
	C[c]	303.7	–7.1	
	D[c]	308.9	–1.9	
9	**A**[d]	55.8	–	**C**
	C[c]	69.4	13.6	

[a] See Scheme 2. [b] Difference between the values of ΔH_f for monomeric form **A** and hydrogen-bonded forms **B**–**D**. [c] Calculated for one molecule in the intermolecularly hydrogen-bonded cyclic dimer. [d] Monomeric form.

TABLE VII
Selected AM1 charge densities (q) and bond orders (p) for preferential forms[a] of compounds **3**, **6** and **7**

Compd	$q(C^5)$	$q(O^5)$	$q(C^5{=}O)$	$q(C^4)$	$q(C^7)$	$q(H^6)$
3**a**	0.325	–0.375	1.7418	–0.185	–	0.277
3b	0.322	–0.385	1.7272	–0.184	–	0.274
3c	0.329	–0.386	1.7311	–0.185	–	0.276
3d	0.322	–0.384	1.7294	–0.185	–	0.275
3e	0.321	–0.388	1.7239	–0.184	–	0.274
3f	0.320	–0.391	1.7191	–0.184	–	0.273
3g	0.321	–0.387	1.7250	–0.184	–	0.274
3h	0.328	–0.386	1.7313	–0.185	–	0.275
3i	0.333	–0.383	1.7328	–0.183	–	0.281
3j	0.320	–0.390	1.7202	–0.184	–	0.273
3k	0.317	–0.395	1.7136	–0.184	–	0.270
6a	0.362	–0.357	1.7403	–0.206	–0.335	0.262
6b	0.364	–0.352	1.7482	–0.212	–0.335	0.264
6c	0.357	–0.347	1.7545	–0.177	–0.350	0.268
6d	0.368	–0.343	1.7638	–0.229	–0.325	0.266
6e	0.362	–0.352	1.7459	–0.208	–0.336	0.264
6f	0.370	–0.342	1.7634	–0.226	–0.335	0.267
6j	0.362	–0.356	1.7416	–0.207	–0.335	0.262
6k	0.359	–0.363	1.7312	–0.202	–0.335	0.261
7a	0.365	–0.387	1.6402	–0.269	–0.360	0.265
7b	0.368	–0.383	1.6492	–0.271	–0.360	0.268
7c	0.368	–0.384	1.6508	–0.271	–0.360	0.277
7d	0.369	–0.383	1.6514	–0.272	–0.361	0.269
7e	0.367	–0.385	1.6456	–0.269	–0.360	0.268
7f	0.371	–0.376	1.6660	–0.275	–0.361	0.272
7g	0.367	–0.385	1.6466	–0.270	–0.360	0.267
7h	0.368	–0.384	1.6509	–0.269	–0.360	0.277
7j	0.366	–0.386	1.6409	–0.267	–0.360	0.266
7k	0.362	–0.390	1.6329	–0.268	–0.360	0.263

[a] See Table VI.

the inspection of correlations of the IR and NMR spectral characteristics with AM1 theoretical data (Table IX) that satisfactory results are obtained, when form **C** for compounds **3**, form **D** for compounds **6** and form **B** for compounds **7** are considered as preferential conformations.

EXPERIMENTAL

Theoretical calculations were performed using the semiempirical AM1 Hamiltonian[17] with program package AMPAC[18]. Geometries were completely optimized.

Melting points were determined on a Boetius micro heating stage (Carl Zeiss Jena) and are uncorrected. Elemental analyses were performed with a CHNS-932 LECO analyzer. Mass spectra of positive ions obtained by electron impact (EI, 70 eV) were taken on an AMD 402 spectrometer (Intectra GmbH). Infrared spectra were measured in $CHCl_3$ or CCl_4 solutions on a Zeiss 80 Specord spectrometer at room temperature using NaCl cells of 0.1, 1.0 and

TABLE VIII
Linear correlations of IR and NMR spectral data[a] with Hammett σ constants for series of compounds **3**, **6** and **7**: $y = \rho\sigma + z$

Compd	*y*	*n*[b]	*r*[c]	*s*[d]	*F*[e]	ρ	*z*
3	ν(C^5=O)	9[f]	0.993	1.23	508	19.93±0.88	1680.7
	δ(H^6)	7[g]	0.924	0.120	29	0.467±0.086	9.31
	δ(C^4)	poor correlation					
	δ(C^5)	10	0.928	0.096	50	0.482±0.068	163.19
6	ν(C^5=O)	8	0.987	1.02	229	11.08±0.73	1673.9
	δ(H^6)	7[h]	0.867	0.183	15	0.532±0.136	8.22
	δ(C^4)	6[i]	0.941	0.343	31	–1.491±0.269	129.82
	δ(C^5)	poor correlation					
	δ(C^7)	7[j]	0.976	0.285	102	0.230±0.023	156.80
7	ν(C^5=O)	10	0.986	1.03	289	12.37±0.73	1631.4
	δ(H^6)	7[k]	0.932	0.137	33	0.644±0.112	10.63
	δ(C^4)	7[l]	0.946	0.164	42	–0.842±0.129	110.03
	δ(C^5)	7[k]	0.928	0.096	31	0.441±0.079	163.05
	δ(C^7)	8	0.895	0.584	24	2.210±0.449	181.64

[a] IR stretching vibrations ν in $CHCl_3$, and NMR chemical shifts δ in $CDCl_3$. [b] The number of compounds used in correlation. [c] Correlation coefficient. [d] Standard deviation. [e] Fisher–Snedecor test for parameters significant at the 95% level. [f] Compound **3h** omitted. [g] Compounds **3h**, **3c** and **3i** omitted. [h] Compound **6d** omitted. [i] Compounds **6a** and **6c** omitted. [j] Compound **6f** omitted. [k] Compound **7d** omitted. [l] Compound **7h** omitted.

5.0 mm thicknesses. The concentrations of solutions were chosen to give absorption in the range 75–85% (estimated concentration: 2×10^{-2} mol/l at 0.1 mm, 1×10^{-2} mol/l at 1.0 mm). The solvents used for measurements were of spectral purity (Uvasol, Merck). The wavenumbers in the region 1800–1500 cm^{-1} were determined with an accuracy of ±0.2 cm^{-1}. The ^1H and ^{13}C NMR spectra (δ in ppm) were recorded for 0.5 mol/l solutions in $CDCl_3$ with TMS as internal standard using a 5 mm tube at 23 °C on a VXR Varian spec-

TABLE IX
Linear correlations of IR and NMR spectral data[a] with AM1 bond orders and atomic charges for series of compounds **3**, **6** and **7**: $y = \rho x + z$

Compd	*y*	*x*	*n*[b]	*r*[c]	*s*[d]	*F*[e]	ρ	*z*
3	ν(C^5=O)	*p*(C^5=O)	8[f]	0.958	2.987	67	1472.428±180.109	–855.609
		q(C^5)	poor correlation					
		q(O^5)	8[f]	0.954	3.124	61	2397.041±307.923	2612.909
	δ(H^6)	*q*(H^6)	7[g]	0.932	0.114	33	153.983±26.745	–32.733
	δ(C^4)	*q*(C^4)	poor correlation					
	δ(C^5)	*q*(C^5)	6[h]	0.991	0.033	228	117.754±7.803	125.493
6	ν(C^5=O)	*p*(C^5=O)	8	0.921	2.501	33	477.555±82.715	840.939
		q(C^5)	8	0.888	2.945	22	1475.604±312.007	1138.816
		q(O^5)	8	0.942	2.148	47	795.777±115.675	1955.641
	δ(H^6)	*q*(H^6)	7[i]	0.977	0.061	105	107.055±10.424	–20.032
	δ(C^4)	*q*(C^4)	7[j]	0.917	0.385	27	76.540±14.872	145.967
	δ(C^5)	*q*(C^5)	6[k]	0.982	0.028	111	36.352±3.447	148.486
	δ(C^7)	*q*(C^7)	poor correlation					
7	ν(C^5=O)	*p*(C^5=O)	9[l]	0.951	1.895	66	867.888±106.547	205.319
		q(C^5)	9[l]	0.961	1.691	85	2559.488±277.304	695.053
		q(O^5)	9[l]	0.921	2.387	39	2373.992±378.868	2548.191
	δ(H^6)	*q*(H^6)	8[l]	0.974	0.088	109	122.971±11.773	–22.201
	δ(C^4)	*q*(C^4)	7[m]	0.900	0.193	21	129.829±28.090	145.224
	δ(C^5)	*q*(C^5)	8	0.927	0.089	36	75.812±12.565	135.284
	δ(C^7)	*q*(C^7)	6[n]	0.901	0.338	17	–4272.30±1027.52	–1356.448

[a] IR stretching vibrations ν in $CHCl_3$, and NMR chemical shifts δ in $CDCl_3$. [b] The number of compounds used in correlation. [c] Correlation coefficient. [d] Standard deviation. [e] Fisher–Snedecor test for parameters significant at the 95% level. [f] Compounds **3f** and **3h** omitted. [g] Compounds **3f**, **3i** and **3h** omitted. [h] Compounds **3c**, **3f**, **3i** and **3h** omitted. [i] Compound **6f** omitted. [j] Compound **6c** omitted. [k] Compounds **6b** and **6d** omitted. [l] Compounds **7c** and **7h** omitted. [m] Compound **7d** omitted. [n] Compounds **7f** and **7k** omitted.

trometer operating at 299.94 MHz frequency for ^{1}H nuclei and at 75.43 MHz for ^{13}C nuclei. For signal assignments, ^{1}H and ^{13}C APT, HETCOR, DQCOSY, DIFNOE and SINEPT[19] (semiselective INEPT) techniques were used.

Isopropyl *N*-Arylmalonamates **3a**–**3k**. General Procedure

Diisopropyl malonate (28.2 g, 0.15 mol) and corresponding aromatic amine (0.1 mol) were heated in a metal bath at 170 °C for 1 h. The reaction mixture was cooled to room temperature and isopropyl alcohol (50 ml) was added with stirring. After 10 min the precipitate was filtered off and the solution diluted with water (50 ml). After cooling the solid was filtered off and recrystallized.

Isopropyl N-(4-methylphenyl)malonamate (**3a**)[20]. Yield 15.8 g (67%); m.p. 82–83 °C (diethyl ether). For $C_{13}H_{17}NO_3$ (235.3) calculated: 66.36% C, 7.28% H, 5.95% N; found: 66.16% C, 7.21% H, 5.71% N. ^{1}H NMR: 1.28 d, 6 H (2 CH_3); 2.30 s, 3 H (4-CH_3); 3.40 s, 2 H (CH_2); 5.09 m, 1 H (CH); 7.09–7.43 m, 4 H (arom); 9.14 s (br), 1 H (NH).

Isopropyl N-(4-bromophenyl)malonamate (**3b**). Yield 22.9 g (76%); m.p. 90–92 °C (isopropyl alcohol–water). For $C_{12}H_{14}BrNO_3$ (300.2) calculated: 48.02% C, 4.70% H, 26.62% Br, 4.67% N; found: 48.23% C, 4.58% H, 26.57% Br, 4.68% N. ^{1}H NMR: 1.28 d, 6 H (2 CH_3); 3.43 s, 2 H (CH_2); 5.10 m, 1 H (CH); 7.40–7.48 m, 4 H (arom); 9.42 s (br), 1 H (NH).

Isopropyl N-(2,3-dichlorophenyl)malonamate (**3c**). Yield 17.1 g (59%); m.p. 65–66 °C (isopropyl alcohol–water). For $C_{12}H_{13}Cl_2NO_3$ (290.2) calculated: 49.68% C, 4.52% H, 24.44% Cl, 4.83% N; found: 49.66% C, 4.49% H, 24.43% Cl, 4.89% N. ^{1}H NMR: 1.31 d, 6 H (2 CH_3); 3.51 s, 2 H (CH_2); 5.16 m, 1 H (CH); 7.20–8.34 m, 3 H (arom); 9.94 s (br), 1 H (NH).

Isopropyl N-(3,4-dichlorophenyl)malonamate (**3d**)[20]. Yield 17.7 g (61%); m.p. 93–95 °C (isopropyl alcohol). For $C_{12}H_{13}Cl_2NO_3$ (290.2) calculated: 49.68% C, 4.52% H, 24.44% Cl, 4.83% N; found: 49.48% C, 4.35% H, 24.22% Cl, 4.80% N. ^{1}H NMR: 1.30 d, 6 H (2 CH_3); 3.44 s, 2 H (CH_2); 5.11 m, 1 H (CH); 7.37–7.60 m, 3 H (arom); 9.51 s (br), 1 H (NH).

Isopropyl N-(3-chloro-4-methylphenyl)malonamate (**3e**). Yield 12.4 g (46%); m.p. 85–87 °C (isopropyl alcohol–water). For $C_{13}H_{16}ClNO_3$ (269.7) calculated: 57.89% C, 5.98% H, 13.14% Cl, 5.19% N; found: 57.85% C, 5.97% H, 13.06% Cl, 5.24% N. ^{1}H NMR: 1.30 d, 6 H (2 CH_3); 2.31 s, 3 H (4-CH_3); 3.42 s, 2 H (CH_2); 5.10 m, 1 H (CH); 7.15–7.64 m, 3 H (arom); 9.31 s (br), 1 H (NH).

Isopropyl N-(4-nitrophenyl)malonamate (**3f**). Yield 9.6 g (36%); m.p. 87–89 °C (isopropyl alcohol–water). For $C_{12}H_{14}N_2O_5$ (266.3) calculated: 54.13% C, 5.30% H, 10.52% N; found: 53.98% C, 5.35% H, 10.32% N. ^{1}H NMR: 1.30 d, 6 H (2 CH_3); 3.49 s, 2 H (CH_2); 5.13 m, 1 H (CH); 7.74–8.22 m, 4 H (arom); 9.86 s (br), 1 H (NH).

Isopropyl N-(4-chlorophenyl)malonamate (**3g**)[20]. Yield 12.3 g (48%); m.p. 90–92 °C (isopropyl alcohol–water). For $C_{12}H_{14}ClNO_3$ (255.7) calculated: 56.37% C, 5.52% H, 13.86% Cl, 5.48% N; found: 56.26% C, 5.51% H, 13.85% Cl, 5.53% N. ^{1}H NMR: 1.30 d, 6 H (2 CH_3); 3.43 s, 2 H (CH_2); 5.11 m, 1 H (CH); 7.27–7.52 m, 4 H (arom); 9.41 s (br), 1 H (NH).

Isopropyl N-(2,4-dichlorophenyl)malonamate (**3h**)[20]. Yield 17.7 g (61%); m.p. 85–87 °C (isopropyl alcohol–water). For $C_{12}H_{13}Cl_2NO_3$ (290.2) calculated: 49.68% C, 4.52% H, 24.44% Cl, 4.83% N; found: 49.68% C, 4.49% H, 24.44% Cl, 4.88% N. ^{1}H NMR: 1.30 d, 6 H (2 CH_3); 3.49 s, 2 H (CH_2); 5.15 m, 1 H (CH); 7.22–8.37 m, 3 H (arom); 9.86 s (br), 1 H (NH).

Isopropyl N-(2,5-dichlorophenyl)malonamate (**3i**). Yield 16.8 g (58%); m.p. 68–70 °C (isopropyl alcohol–water). For $C_{12}H_{13}Cl_2NO_3$ (290.2) calculated: 49.68% C, 4.52% H, 24.44% Cl,

4.83% N; found: 49.87% C, 4.48% H, 24.17% Cl, 4.79% N. ^{1}H NMR: 1.29 d, 6 H (2 CH_3); 3.47 s, 2 H (CH_2); 5.13 m, 1 H (CH); 6.99–8.48 m, 3 H (arom); 9.91 s (br), 1 H (NH).

Isopropyl N-phenylmalonamate (**3j**)[20,21]. Yield 15.0 g (68%); m.p. 86–87 °C (isopropyl alcohol–water). For $C_{12}H_{15}NO_3$ (221.3) calculated: 65.14% C, 6.83% H, 6.33% N; found: 65.46% C, 6.55% H, 6.53% N. ^{1}H NMR: 1.28 d, 6 H (2 CH_3); 3.43 s, 2 H (CH_2); 5.11 m, 1 H (CH); 7.09–7.57 m, 5 H (arom); 9.29 s (br), 1 H (NH).

Isopropyl N-[4-(dimethylamino)phenyl]malonamate (**3k**). Yield 9.5 g (36%); m.p. 82–83 °C (isopropyl alcohol–water). For $C_{14}H_{20}N_2O_3$ (264.3) calculated: 63.62% C, 7.63% H, 10.60% N; found: 63.43% C, 7.58% H, 10.31% N. ^{1}H NMR: 1.28 d, 6 H (2 CH_3); 2.90 s, 6 H ($N(CH_3)_2$); 3.39 s, 2 H (CH_2); 5.06 m, 1 H (CH); 6.68–7.32 m, 4 H (arom); 9.99 s (br), 1 H (NH).

Isopropyl *N*-Aryl-2-[bis(methylsulfanyl)methylidene]malonamates **6a**–**6g**, **6j**, **6k** and Isopropyl *N*-Aryl-2-(1,3-dithiolan-2-ylidene)malonamates **7a**–**7h**, **7j**, **7k**. General Procedure

Sodium hydride (0.48 g, 0.02 mol) was added portionwise, during 10 min and at 10 °C, to a solution of isopropyl *N*-arylmalonamate **3** (0.01 mol) and carbon disulfide (0.76 g, 0.01 mol) in dry dimethyl sulfoxide (25 ml) under nitrogen atmosphere while stirring. The stirring was continued at the same temperature for 2 h and then methyl iodide (2.84 g, 0.02 mol) or 1,2-dibromoethane (1.88 g, 0.01 mol) was added dropwise maintaining the temperature below 10 °C. The stirring was continued for another 3 h. The reaction mixture was then poured into ice/water (90 ml). The resulting solid was filtered off and recrystallized.

Isopropyl 2-[bis(methylsulfanyl)methylidene]-N-(4-methylphenyl)malonamate (**6a**). Yield 2.3 g (68%); m.p. 175–176.5 °C (isopropyl alcohol). For $C_{16}H_{21}NO_3S_2$ (339.5) calculated: 56.61% C, 6.24% H, 4.13% N, 18.89% S; found: 56.45% C, 6.54% H, 3.95% N, 18.69% S. ^{1}H NMR: 1.32 d, 6 H (2 CH_3); 2.32 s, 3 H (4-CH_3); 2.45 s, 6 H (2 SCH_3); 5.15 m, 1 H (CH); 7.12–7.47 m, 4 H (arom); 8.06 s (br), 1 H (NH).

Isopropyl 2-[bis(methylsulfanyl)methylidene]-N-(4-bromophenyl)malonamate (**6b**). Yield 2.1 g (52%); m.p. 223–224 °C (isopropyl alcohol). For $C_{15}H_{18}BrNO_3S_2$ (404.4) calculated: 44.56% C, 4.49% H, 19.76% Br, 3.46% N, 15.86% S; found: 44.60% C, 4.68% H, 19.50% Br, 3.30% N, 15.76% S. ^{1}H NMR: 1.31 d, 6 H (2 CH_3); 2.46 s, 6 H (2 SCH_3); 5.15 m, 1 H (CH); 7.45 m, 4 H (arom); 8.22 s (br), 1 H (NH).

Isopropyl 2-[bis(methylsulfanyl)methylidene]-N-(2,3-dichlorophenyl)malonamate (**6c**). Yield 1.8 g (46%); m.p. 117–118 °C (isopropyl alcohol). For $C_{15}H_{17}Cl_2NO_3S_2$ (394.3) calculated: 45.69% C, 4.35% H, 17.98% Cl, 3.55% N, 16.26% S; found: 45.91% C, 4.27% H, 17.81% Cl, 3.29% N, 16.31% S. ^{1}H NMR: 1.32 d, 6 H (2 CH_3); 2.48 s, 6 H (2 SCH_3); 5.18 m, 1 H (CH); 7.22–8.40 m, 3 H (arom); 8.73 s (br), 1 H (NH).

Isopropyl 2-[bis(methylsulfanyl)methylidene]-N-(3,4-dichlorophenyl)malonamate (**6d**). Yield 1.6 g (41%); m.p. 129–131 °C (isopropyl alcohol). For $C_{15}H_{17}Cl_2NO_3S_2$ (394.3) calculated: 45.69% C, 4.35% H, 17.98% Cl, 3.55% N, 16.26% S; found: 45.58% C, 4.44% H, 17.78% Cl, 3.39% N, 16.15% S. ^{1}H NMR: 1.32 d, 6 H (2 CH_3); 2.47 s, 6 H (2 SCH_3); 5.15 m, 1 H (CH); 7.38–7.85 m, 3 H (arom); 8.40 s (br), 1 H (NH).

Isopropyl 2-[bis(methylsulfanyl)methylidene]-N-(3-chloro-4-methylphenyl)malonamate (**6e**). Yield 1.5 g (40%); m.p. 126–128 °C (isopropyl alcohol). For $C_{16}H_{20}ClNO_3S_2$ (373.9) calculated: 51.40% C, 5.39% H, 9.48% Cl, 3.75% N, 17.15% S; found: 51.22% C, 5.39% H, 9.27% Cl, 3.51% N, 17.04% S. ^{1}H NMR: 1.31 d, 6 H (2 CH_3); 2.33 s, 3 H (4-CH_3); 2.46 s, 6 H (2 SCH_3); 5.15 m, 1 H (CH); 7.15–7.68 m, 3 H (arom); 8.19 s (br), 1 H.

Isopropyl 2-[bis(methylsulfanyl)methylidene]-N-(4-nitrophenyl)malonamate (**6f**). Yield 1.3 g (35%); m.p. 182–183 °C (isopropyl alcohol). For $C_{15}H_{18}N_2O_5S_2$ (370.5) calculated: 48.63% C, 4.90% H, 7.56% N, 17.31% S; found: 48.72% C, 5.01% H, 7.56% N, 17.39% S. ^{1}H NMR: 1.33 d, 6 H (2 CH_3); 2.49 s, 6 H (2 SCH_3); 5.17 m, 1 H (CH); 7.77–8.22 m, 4 H (arom); 8.86 s (br), 1 H (NH).

Isopropyl 2-[bis(methylsulfanyl)methylidene]-N-(4-chlorophenyl)malonamate (**6g**). Yield 1.7 g (47%); m.p. 200–201 °C (isopropyl alcohol). For $C_{15}H_{18}ClNO_3S_2$ (359.9) calculated: 50.06% C, 5.04% H, 9.85% Cl, 3.89% N, 17.82% S; found: 49.87% C, 4.96% H, 9.72% Cl, 3.71% N, 17.90% S. ^{1}H NMR: 1.30 d, 6 H (2 CH_3); 2.44 s, 6 H (2 SCH_3); 5.14 m, 1 H (CH); 7.25–7.52 m, 4 H (arom); 8.16 s (br), 1 H (NH).

Isopropyl 2-[bis(methylsulfanyl)methylidene]-N-phenylmalonamate (**6j**). Yield 2.2 g (68%); m.p. 150–151 °C (isopropyl alcohol). For $C_{15}H_{19}NO_3S_2$ (325.5) calculated: 55.36% C, 5.88% H, 4.30% N, 19.70% S; found: 55.25% C, 5.85% H, 4.15% N, 19.59% S. ^{1}H NMR: 1.31 d, 6 H (2 CH_3); 2.45 s, 6 H (2 SCH_3); 5.15 m, 1 H (CH); 7.10–7.58 m, 5 H (arom); 8.14 s (br), 1 H (NH).

Isopropyl 2-[bis(methylsulfanyl)methylidene]-N-[4-(dimethylamino)phenyl]malonamate (**6k**). Yield 1.6 g (43%); m.p. 154–157 °C (isopropyl alcohol). For $C_{17}H_{24}N_2O_3S_2$ (368.5) calculated: 55.41% C, 6.56% H, 7.60% N, 17.40% S; found: 55.40% C, 6.81% H, 7.81% N, 17.68% S. ^{1}H NMR: 1.30 d, 6 H (2 CH_3); 2.45 s, 6 H (2 SCH_3); 2.95 s, 6 H ($N(CH_3)_2$); 5.14 m, 1 H (CH); 6.64–7.43 m, 4 H (arom); 7.92 s (br), 1 H (NH).

Isopropyl 2-(1,3-dithiolan-2-ylidene)-N-(4-methylphenyl)malonamate (**7a**). Yield 2.1 g (62%); m.p. 110–112 °C (isopropyl alcohol). For $C_{16}H_{19}NO_3S_2$ (337.5) calculated: 56.95% C, 5.68% H, 4.15% N, 19.00% S; found: 56.73% C, 5.75% H, 4.03% N, 19.05% S. ^{1}H NMR: 1.49 d, 6 H (2 CH_3); 2.29 s, 3 H (4-CH_3); 3.31 s, 4 H (2 CH_2); 5.24 m, 1 H (CH); 7.07–7.49 m, 4 H (arom); 10.40 s (br), 1 H (NH).

Isopropyl N-(4-bromophenyl)-2-(1,3-dithiolan-2-ylidene)malonamate (**7b**). Yield 2.1 g (52%); m.p. 146–148 °C (isopropyl alcohol). For $C_{15}H_{16}BrNO_3S_2$ (402.3) calculated: 44.78% C, 4.01% H, 19.86% Br, 3.48% N, 15.94% S; found: 44.63% C, 3.96% H, 19.71% Br, 3.53% N, 15.96% S. ^{1}H NMR: 1.43 d, 6 H (2 CH_3); 3.34 s, 4 H (2 CH_2); 5.25 m, 1 H (CH); 7.42–7.54 m, 4 H (arom); 10.72 s (br), 1 H (NH).

Isopropyl N-(2,3-dichlorophenyl)-2-(1,3-dithiolan-2-ylidene)malonamate (**7c**). Yield 1.7 g (43%); m.p. 186–188 °C (isopropyl alcohol). For $C_{15}H_{15}Cl_2NO_3S_2$ (392.3) calculated: 45.92% C, 3.85% H, 18.07% Cl, 3.57% N, 16.35% S; found: 45.73% C, 3.73% H, 17.96% Cl, 3.31% N, 16.41% S. ^{1}H NMR: 1.43 d, 6 H (2 CH_3); 3.35 s, 4 H (2 CH_2); 5.30 m, 1 H (CH); 7.25–8.35 m, 3 H (arom); 10.90 s (br), 1 H (NH).

Isopropyl N-(3,4-dichlorophenyl)-2-(1,3-dithiolan-2-ylidene)malonamate (**7d**). Yield 1.8 g (46%); m.p. 119–121 °C (isopropyl alcohol). For $C_{15}H_{15}Cl_2NO_3S_2$ (392.3) calculated: 45.92% C, 3.85% H, 18.07% Cl, 3.57% N, 16.35% S; found: 45.69% C, 3.56% H, 18.05% Cl, 3.33% N, 16.20% S. ^{1}H NMR: 1.43 d, 6 H (2 CH_3); 3.35 s, 4 H (2 CH_2); 5.24 m, 1 H (CH); 7.32–7.94 m, 3 H (arom); 10.89 s (br), 1 H (NH).

Isopropyl N-(3-chloro-4-methylphenyl)-2-(1,3-dithiolan-2-ylidene)malonamate (**7e**). Yield 1.6 g (43%); m.p. 115–116.5 °C (isopropyl alcohol). For $C_{16}H_{18}ClNO_3S_2$ (371.9) calculated: 51.67% C, 4.88% H, 9.53% Cl, 3.77% N, 17.24% S; found: 51.68% C, 4.83% H, 9.49% Cl, 3.52% N, 17.15% S. ^{1}H NMR: 1.43 d, 6 H (2 CH_3); 2.32 s, 3 H (4-CH_3); 3.34 s, 4 H (2 CH_2); 5.26 m, 1 H (CH); 7.13–7.76 m, 3 H (arom); 10.62 s (br), 1 H (NH).

Isopropyl 2-(1,3-dithiolan-2-ylidene)-N-(4-nitrophenyl)malonamate (**7f**). Yield 2.0 g (54%); m.p. 225–226 °C (isopropyl alcohol). For $C_{15}H_{16}N_2O_5S_2$ (368.4) calculated: 48.90% C, 4.38% H,

7.60% N, 17.41% S; found: 48.92% C, 4.64% H, 7.65% N, 17.40% S. ^{1}H NMR: 1.43 d, 6 H (2 CH_3); 3.37 s, 4 H (2 CH_2); 5.26 m, 1 H (CH); 7.78–8.18 m, 4 H (arom); 11.32 s (br), 1 H (NH).

Isopropyl N-(4-chlorophenyl)-2-(1,3-dithiolan-2-ylidene)malonamate (**7g**). Yield 1.6 g (45%); m.p. 157–159 °C (isopropyl alcohol). For $C_{15}H_{16}ClNO_3S_2$ (357.9) calculated: 50.34% C, 4.51% H, 9.91% Cl, 3.91% N, 17.92% S; found: 50.70% C, 4.20% H, 9.73% Cl, 3.66% N, 17.85% S. ^{1}H NMR: 1.43 d, 6 H (2 CH_3); 3.34 s, 4 H (2 CH_2); 5.25 m, 1 H (CH); 7.25–7.59 m, 4 H (arom); 10.72 s (br), 1 H (NH).

Isopropyl N-(2,4-dichlorophenyl)-2-(1,3-dithiolan-2-ylidene)malonamate (**7h**). Yield 1.6 g (41%); m.p. 151–152 °C (isopropyl alcohol). For $C_{15}H_{15}Cl_2NO_3S_2$ (392.3) calculated: 45.92% C, 3.85% H, 18.07% Cl, 3.57% N, 16.35% S; found: 45.69% C, 3.56% H, 17.95% Cl, 3.33% N, 16.21% S. ^{1}H NMR: 1.43 d, 6 H (2 CH_3); 3.35 s, 4 H (2 CH_2); 5.32 m, 1 H (CH); 7.20–8.49 m, 3 H (arom); 10.96 s (br), 1 H (NH).

Isopropyl 2-(1,3-dithiolan-2-ylidene)-N-phenylmalonamate (**7j**). Yield 1.7 g (53%); m.p. 121–123 °C (isopropyl alcohol). For $C_{15}H_{17}NO_3S_2$ (323.4) calculated: 55.70% C, 5.30% H, 4.33% N, 19.83% S; found: 55.60% C, 5.17% H, 4.21% N, 19.78% S. ^{1}H NMR: 1.42 d, 6 H (2 CH_3); 3.32 s, 4 H (2 CH_2); 5.25 m, 1 H (CH); 7.05–7.57 m, 5 H (arom); 10.54 s (br), 1 H (NH).

Isopropyl N-[4-(dimethylamino)phenyl]-2-(1,3-dithiolan-2-ylidene)malonamate (**7k**). Yield 1.4 g (38%); m.p. 141–142 °C (isopropyl alcohol). For $C_{17}H_{22}N_2O_3S_2$ (366.5) calculated: 55.71% C, 6.05% H, 7.64% N, 17.50% S; found: 55.65% C, 5.91% H, 7.52% N, 17.71% S. ^{1}H NMR: 1.40 d, 6 H (2 CH_3); 2.89 s, 6 H ($N(CH_3)_2$); 3.30 s, 4 H (2 CH_2); 5.20 m, 1 H (CH); 6.68 d, 2 H (arom); 7.39 d, 2 H (arom); 10.22 s (br), 1 H (NH).

Isopropyl *N*-(3,4-Dichlorophenyl)-2-(4,9-dioxo-4,9-dihydronaphtho[2,3-*d*][1,3]dithiol-2-ylidene)malonamate (**8**)

Sodium hydride (1.44 g, 0.06 mol) was added portionwise, at 10 °C and during 30 min, to a solution of isopropyl malonamate (**3d**; 8.70 g, 0.03 mol) and carbon disulfide (2.28 g, 0.03 mol) in dry dimethyl sulfoxide (100 ml) under nitrogen and while stirring and cooling. The stirring was continued for 4 h at the same temperature. Then a solution of 2,3-dichloro-1,4-naphthoquinone (6.81 g, 0.03 mol) in dimethyl sulfoxide (30 ml) was added dropwise maintaining the temperature below 10 °C and stirring was continued for another 3 h. The reaction mixture was then poured into ice/water (300 ml). The solid was filtered off and recrystallized to afford 12.6 g (78%) of **8**, m.p. 261–263 °C (toluene). For $C_{23}H_{15}Cl_2NO_5S_2$ (520.4) calculated: 53.08% C, 2.91% H, 13.62% Cl, 2.69% N, 12.32% S; found: 52.90% C, 2.92% H, 13.83% Cl, 2.70% N, 12.25% S. IR: 3447, 1677, 1664, 1623, 1582, 1564, 1533, 1479, 1418, 1279, 1099. ^{1}H NMR: 1.53 d, 6 H (2 CH_3); 5.34 m, 1 H (CH); 7.34–8.19 m, 7 H (arom); 11.01 s (br), 1 H (NH). MS (EI), *m/z* (rel.%): 519 (44) [M^+], 359 (100) [M^+ – $NHC_6H_3Cl_2$], 317 (100), 301 (14), 279 (29), 233 (4), 189 (8), 161 (2), 104 (6), 85 (9), 76 (5).

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